Rev. Real Academia de Ciencias. Zaragoza. **79:** 7–52, (2024). ISSN: 0370-3207

Designing polymer materials with dynamic bonds

Jesús del Barrio Lasheras

Instituto de Nanociencia y Materiales de Aragón (INMA)
CSIC-Universidad de Zaragoza
50009 Zaragoza, España
Departamento de Química Orgánica
Universidad de Zaragoza, 50009 Zaragoza, Spain
`jdb529@unizar.es`

Premio a la Investigación de la Academia 2024. Sección de Químicas

Abstract

Polymeric materials have revolutionized modern life, from electronics to biomedical devices, thanks to breakthroughs in synthesis and engineering. Yet, traditional polymers –built on covalent static networks– pose challenges in, for example, degradation and energy-intensive recycling. Now, interest in dynamic chemistries has enabled reconfigurable polymer systems that respond to external stimuli, supporting applications such as chemical recycling and adaptive materials. Dynamic bonds, including supramolecular and dynamic covalent interactions, provide tools for designing responsive materials with tailored and reversible structures, allowing controlled adaptations in response to environmental changes. This article summarizes key design strategies for integrating dynamic bonds into polymeric materials, and highlights major advancements and emerging trends in this field.

1 Introduction

The development and use of polymeric materials, driven by advancements in their synthesis, engineering, and manufacturing, have profoundly transformed modern society.[1] Since H. Staudinger's Macromolecular Hypothesis in 1920,[2] polymers have evolved into one of the largest segments of the materials industry, finding diverse applications across a number of fields from low-cost electronics to implantable biomedical devices, and lightweight parts for vehicles and airplanes. However, many *conventional* polymers rely on high-molecular-weight *static* networks, which can sometimes result in issues such as undesirable or uncontrolled degradation and the requirement of energy-intensive processes for their recycling and reprocessing. In other words, common *traditional* polymers are frequently designed as passive structures, focusing on enhancing their mechanical, thermal, or electronic properties. These *traditional* polymeric materials typically exhibit permanent non-reconfigurable covalent bonds, with efforts concentrated on preventing the breakage of these bonds under operating conditions, as such, breakage usually results in an undesirable decline in the properties and performance of the material.

Over the past few decades, there has been renewed interest in dynamic chemistries, where specific bonds or interactions can be broken, reformed, or reconfigured upon exposure to certain environmental factors.[3,4] The ability of dynamic bonds to isomerize, rearrange, break and reform allows the creation of structurally distinct dynamic polymer systems that can adapt their structure or composition and potentially demonstrate a controlled macroscopic response to external stimuli. The use of dynamic or reconfigurable *bond-making chemistries* also represents an opportunity to revise current strategies for designing and constructing polymeric materials, with a view towards addressing critical challenges in, for example, chemical recycling and innovative biomedical materials.

The history of reversible processes within polymer science is extensive and diverse, and encompasses phenomena such as ring-chain equilibria and the utilization of dynamic equilibria between propagating radicals and dormant species in controlled radical polymerizations.[5] A number of reversible covalent and non-covalent interactions (as well as isomerizable or rearrangeable functional moieties), have been successfully integrated with diverse organic building blocks –of low and high molecular weight– to create adaptive and stimuli-responsive materials (Figure 1). Some examples of these building blocks include end-functionalized oligomers and polymers, block-copolymers, polymer network precursors and reactive liquid crystals (LCs) to name just a few. Surely, the reader will recognize that a wide range of materials inherently possess the ability to exhibit stimuli-responsive behavior through various mechanisms. Indeed, phase segregation and phase transitions, including the glass transition and the isotropization of LCs, are central to numerous applications such as actuators, adaptive surfaces, re-healable materials and substance delivery systems.[6,7] Unlike the previous examples, the main idea behind polymeric materials exhibiting a dynamic architecture, as discussed in this brief revision, is that their subcomponents can rearrange due to the responsive nature of specific dynamic bonds. This rearrangement leads to changes in structure or connectivity, resulting in a controlled macroscopic response. Therefore, the careful selection of dynamic bonds and specific (macro)molecular building blocks enables the creation of materials with tailored responses for particular applications.

In this Review, a *dynamic* bond is defined as any type of bond capable breaking and reforming, or rearranging, typically under equilibrium conditions. Consequently, the term *dynamic* includes two broad families of bonds: supramolecular (i) and dynamic covalent interactions (ii). Supramolecular or non-covalent bonds typically include hydrogen bonding, π–π stacking, metal-ligand coordination, macrocyclic host-guest complexation and halogen bonding. A dynamic covalent bond, in contrast, can be viewed as a reversible covalent bond that breaks and reforms cleanly, without causing any significant side reaction. Therefore, replacing a covalent bond that connects specific subcomponents or monomeric units within a larger macromolecular construct by a dynamic bond may produce a structurally dynamic material capable of exhibiting stimuli-responsive behavior (Table 1). The two broad families (i) and (ii) of dynamic bonds share some common characteristics such as the ability to exchange, and the fact that their end-state composition can be influenced to some extent by external factors such as temperature, concentration, etc. Supramolecular interactions (ii) are generally in equilibrium, while dynamic covalent bonds (i) typically require the presence of a catalyst or specific stimulation to revert.

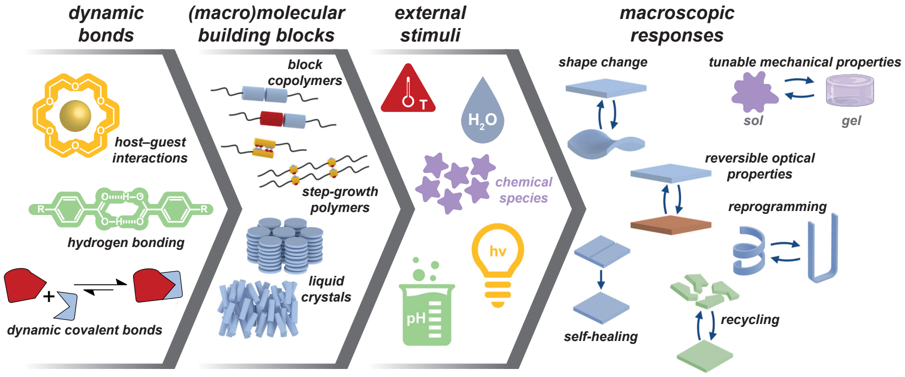


Figure 1: Rationale for pursuing the integration of dynamic bonds into (macro)molecular materials. Adapted from ref. 6 Copyright 2021 The Authors.

For the materials scientist, the molecular toolbox available for designing stimuli-responsive materials is broad and varied (Figure 1). The dynamic bond serves as a crucial element within this toolkit, enabling the adjustment of specific thermodynamic and kinetic parameters that ultimately dictate the macroscopic behavior of structurally dynamic polymers.[8] Of course, other factors must be considered when selecting the appropriate dynamic bond for a specific materials application such as the directionality of the complementary components and the solubility of the binding motifs. These aspects, along with other design features related to incorporating dynamic bonds into (macro)molecular architectures will be discussed in the following sections.

1.1 Supramolecular non-covalent interactions

In order to look at the characteristics of polymeric structures incorporating dynamic non-covalent bonds (i.e. supramolecular polymers), certain considerations are necessarily required for their definition. Meijer *et al.* has proposed the following.[9]

Supramolecular polymers are defined as polymeric arrays of monomeric units that are brought together by reversible and directional secondary interactions, resulting in polymeric properties in dilute and concentrated solutions, as well as in the bulk. The monomeric units of the supramolecular polymers themselves do not possess a repetition of chemical fragments.

dynamic bond	**binding motif**	**(macro)molecular architecture**	**conditions**	**material property/ application**	**ref.**
hydrogen bonding	carboxylic acid dimer	liquid crystal network	solvent-free ambient temp.	controlled deformation in response to moisture	[180]
dynamic covalent	arylboronate–diol	star tetra-PEG network	aqueous ambient temp.	glucose responsive hydrogels for therapeutic encapsulation and release	[154]
host-guest complexation	CB[8]–viologen–naphthyl ternary complex	supramolecular amphiphilic block copolymer	aqueous ambient temp.	multi-responsive micellar encapsulats for therapeutic transport and release	[66]
dynamic covalent	Zn catalyzed transesterification	epoxy/acid and epoxy/anhydride polymer network	solvent-free $100 - 250\,^{\circ}\mathrm{C}$	maleable and reparable crosslinked polymer networks	[103]

Table 1: Selected examples of structurally dynamic polymer materials.

The directionality and strength of the supramolecular bonding are important features of systems that can be regarded as polymers and that behave according to well-established theories of polymer physics.

This definition focuses exclusively on behavior typical of supramolecular polymers from relatively low molecular weight subcomponents (Figure 2d), but macromer-based supramolecular systems should also be considered. Examples of these materials include telechelic macromonomers reversibly bound within the main chain of a larger supramolecular polymeric species (Figure 2f), or block copolymers where disparate blocks are connected through non-covalent interactions (Figure 2e). These examples employ the same specific interactions as small molecule monomers and can potentially be described using similar established theories.

With this definition in hand, it is possible to review some of the general aspects associated with the incorporation of supramolecular bonds into (macro)molecular structures. In the simplest scenario, useful monomers, either small molecules or macromers, leading to linear structures are necessarily bis-functional and the linking can be of self-complementary or complementary in nature. Self-complementary motifs are capable of binding either through an A:A or A:B motif. The latter generally consists of molecules capable of associating through a double-sided functional structures (e.g. urea stacking promoted by hydrogen bonding and π–π stacking). Comparatively, complementary interactions can be either two-component binding through an A:B motif, or even three-component (for example A:B:A, whereby component B is required for association of components A).

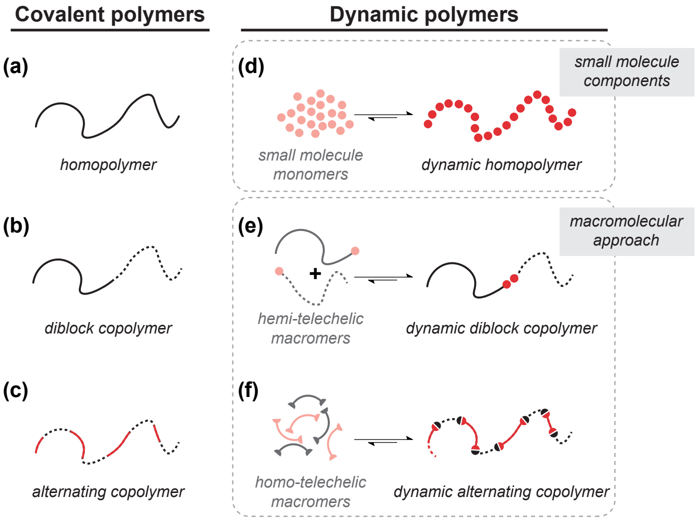


Figure 2: Schematic representation of a covalent homopolymer (a), block copolymer (b), alternating copolymer (c), and their dynamic counterparts (d–f).

Following the traditional condensation polymerization model all known structures of traditional polymers, including linear homo- and block copolymers, crosslinked networks, graft copolymers, comb and (hyper)branched polymers are accessible in supramolecular polymers.[10] With linear supramolecular polymers specifically the degree of polymerization, DP, is associated with the stability or strength of the non-covalent interactions employed between monomeric units and the concentration.[11] If non-cooperativity in the supramolecular polymerization is assumed and the association constant (K_a) between the monomers is known, it is possible to calculate the theoretical DP of a supramolecular polymer according to the Carother's equation.[12,13] The DP is significantly influenced by K_a and the concentration. According to a theoretical framework by Ciferri,[10,14] a relatively high association constant (e.g., $K_a > 10^5\,\mathrm{M}^{-1}$) between monomers in solution is essential for obtaining polymers with high molecular weight when monomer concentrations are in the hundreds of millimolar to molar range. This high molecular weight is crucial for achieving significant mechanical properties or stimuli-responsive behavior.

Another important characteristic of the dynamic supramolecular bond is the timescale on which the bond exists, defined by the rate of monomer association (k_{on}) and dissociation (k_{off}). These kinetic parameters, related to the equilibrium constant ($K_a = k_{\mathrm{on}} \cdot k_{\mathrm{off}}^{-1}$), are crucial in determining, for example, the speed at which the material responds to specific stimulation. True dynamic supramolecular materials must be reversible on experimental time scales. A physical model developed by Cates in the late 1980s for worm-like micellar systems predicts the viscoelastic properties of supramolecular polymers by accounting for both the stability and kinetics of non-covalent interactions between monomers.[15,16] Such a model has been shown to effectively describe the behavior of a broad range of non-covalent crosslinked materials, including the viscoelastic behavior of reversible self-complementary 2-ureido-4[1*H*]-pyrimidinones UPy-based supramolecular polymers.[17] Together, the thermodynamics and kinetics of the dynamic bond significantly influence both the mechanical properties of the supramolecular polymer system and its ability to produce a macroscopic response.

The toolkit of non-covalent dynamic bonds encompasses a variety of interactions including, but not limited to, π–π stacking, hydrogen bonding, halogen bonding, metal-ligand coordination and macrocyclic host-guest complexation (Figure 3). These relatively weak dynamic bonds are typically in equilibrium and, therefore, they are highly responsive to thermal conditions, solvents, reagents, and concentration. Such factors can indeed be leveraged to create dynamic materials that are sensitive to various stimuli.

Hydrogen bonding is crucial in many natural and manmade supramolecular materials. Such an interaction is key to the three-dimensional structure and assembly of both DNA and RNA, where its directionality, specificity and ability to work in a concerted fashion are of fundamental importance –indeed, the combination of multiple base pairs and π–π stacking enables the system to overcome the competition by water molecules. These bonds are certainly not the strongest of the non-covalent interactions (Figure 3), however, due to

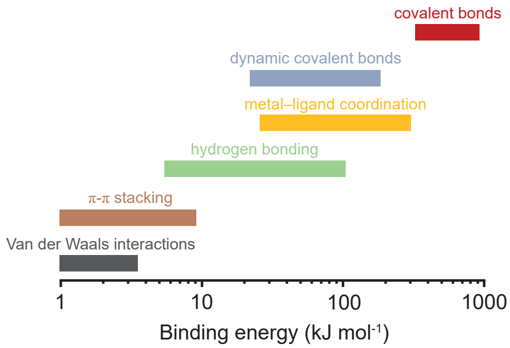


Figure 3: Typical binding energies for different types of bonds and interactions. Adapted with permission from ref 4. Copyright 2021 American Chemical Society.

their directionality and specificity, it is possible to readily design binding motifs capable of accepting and donating, or both, multiple hydrogen bonds simultaneously, which greatly enhances their stability (i.e. K_a).[18] As with single hydrogen bonds, the strength of the resulting interaction is affected by several factors: (i) the nature of the donor, D, and acceptor, A (i.e. angle between D and A, for example), (ii) the solvent, and (iii) the configuration of the donor and acceptor sites (e.g. a different binding strength will be provided by an array of DAAD *vs.* that of DADA). When designing multiple hydrogen bonding units it is important to take into consideration secondary attraction and repulsion between neighboring interactions. As demonstrated in Figure 4, these secondary interactions can greatly alter the K_a leading to a difference of more than two orders of magnitude between the ADA-DAD motif (Figure 4a) and the AAA-DDD motif (Figure 4c).[19]

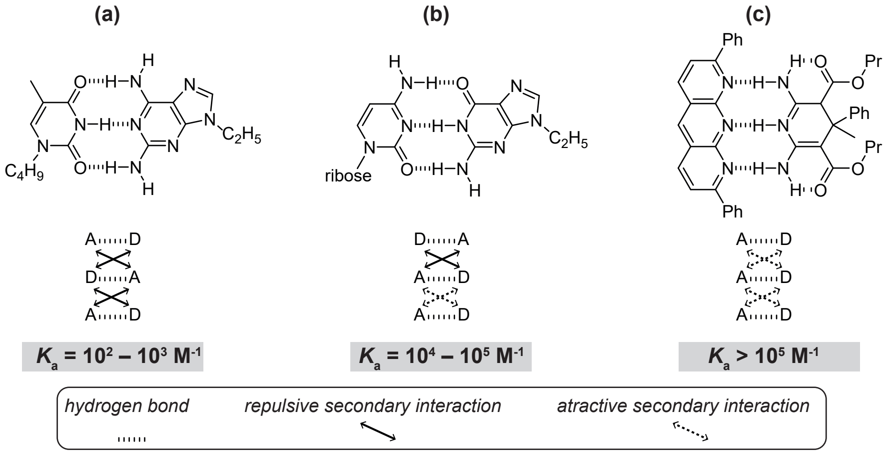
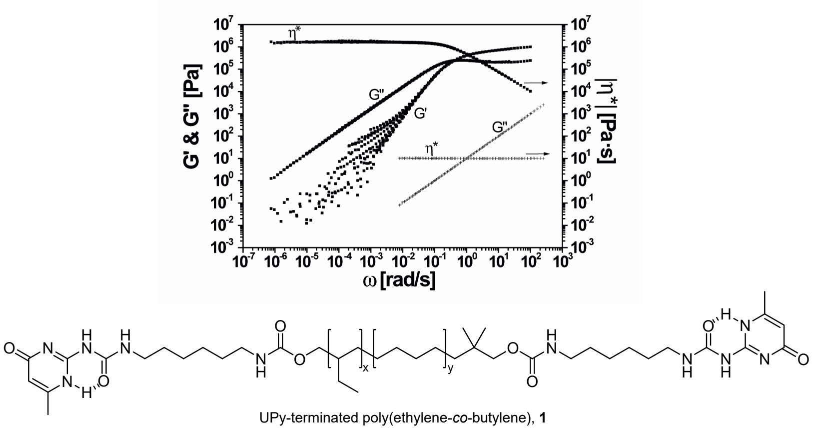


Figure 4: Selected examples of multiple hydrogen bonding motifs.

There have been a large number of multiple-hydrogen bonding arrays reported in the literature over the past three decades.[9,10,20] Each has their own characteristics, ranging from the quintessential quadruple hydrogen bonding unit UPy, an AADD self-complementary array synthesized in a simple one-step process from commercially available isocytosines,[21] which exhibits relatively high dimerization (ca. $10^7 - 10^8\,\mathrm{M}^{-1}$) constants in chloroform, to the more complex pairs produced by Gong and co-workers, which show exceptionally high stability in organic solvents,[22,23] and, in some recent cases, even in aqueous media.[24]

Perhaps the most studied and applied hydrogen bonding unit is that of the UPy-derived family of polymers. Meijer and co-workers have produced a large volume of research in UPy dimerization and its tautomerization to selectively form an A:B complementary binding pair with 2,7-diamido-1,8-napthyridine, NaPy.[25] They demonstrated the assembly of UPy-telechelic poly(ethylene-co-butylene), pEB, prepared *via* post-polymerization functionalization of hydroxy-telechelic pEB (Figure 5).[26] The assembly of these low molecular weight polymers drastically alters the materials properties, converting the starting material from a viscous liquid to an elastic solid after the functionalization with UPy motifs. This demonstrates the versatility of supramolecular polymers as they exhibit properties akin to traditional covalent macromolecules while providing the facile processability from the low melt viscosities of oligomers.



UPy-terminated poly(ethylene-*co*-butylene), **1**

Figure 5: Master curves (top) of dynamic melt viscosity (η^*), storage (G') and loss (G'') moduli corresponding to UPy-pEB-UPy (black squares) and hydroxyl-telechelic pEB (gray crosses), and chemical structure of UPy-pEB-UPy (bottom). Adapted with permission from ref 26. Copyright 2000 John Wiley & Sons, Inc.

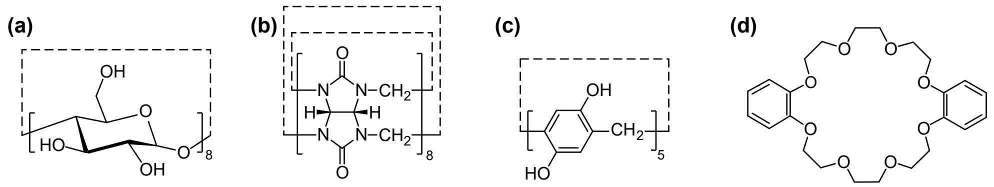
In another study Meijer and co-workers investigated the self-assembly of UPy- and NaPy-telechelic poly(octene) macromonomers which were prepared by ring opening methathesis polymerization, ROMP, using bis-functional chain transfer agents, CTAs.[27] They demonstrated the development of a facile method for the preparation of a range of polymers with end-group fidelity of exactly two that can form supramolecular homo- and block-copolymers using controlled polymerization and simple functional CTAs. They also demonstrated the importance of end-group fidelity as this system exhibited a high dependence of specific viscosity on concentration, comparable to small molecule supramolecular polymers. Interestingly, the materials in the previous examples exhibited much lower dependencies (on concentration, for example), which is due to the presence of some unfunctionalized end-groups leading to chain stoppers that drastically decrease the apparent DP.

Despite the impressive K_a values reported for many of the previous systems and their utility in forming supramolecular materials, their exceptional self-assembly behavior is perhaps restricted to non-polar solvents or the hydrophobic domains within compartmentalized structures. This is because K_a values decrease significantly in polar solvents due to competition from solvent hydrogen bonding. In contrast, metal-ligand coordination has been used in aqueous as well as organic media in a variety of systems. The dynamic nature of these interactions is highly variable. Some metal-ligand coordination –for example, certain cases of Ru(II)-based systems– do not show reversibility on experimental timescales and,[28] therefore cannot be considered dynamic in the definition used above. This feature, nevertheless is interesting as it enables the creation of materials that closely resemble traditional polymers but with latent, chemically responsive capabilities. Particularly with this type of interaction, it is crucial to make careful choices when designing a system, as the selection of metal ion and ligand significantly impacts the stability of the bond and its responsiveness due to varying binding energies (Figure 3).

Some of the most frequently used metal ions include Fe, Ru, Mn, Os, Pt, Ir, Co, Ni, Zn and Cd, and these are normally used in their low oxidation states. Schubert and co-workers reported that diblock homopolymers made from terpyridine ligands and Fe(II) exhibit higher thermal stability than those based on Ru(II).[29] The same group exploited later the terpyridine-based complexation and noted that diblock homopolymers complexed with Zn(II) degrade readily in both acidic and basic conditions, whereas analogous polymers complexed with Ni(II) remain unaffected by pH changes.[30] Taking these ideas into account, a comprehensive library of metallo-supramolecular systems was later developed, which included small molecules, and semi-telechelic and telechelic macromers, all featuring terpyridine ligands as end-groups.[30] One particularly interesting case involved the post-polymerization assembly of terpyridine-functionalized semi-telechelic polyethylene oxide (pEO) and pEB macromers, which resulted in the formation of metallo-supramolecular block copolymers. Schubert and co-workers further advanced this field by developing a terpyridine-functionalized initiator for nitroxide-mediated polymerization (NMP), yielding semi-telechelic polystyrene. Additionally, they devised a method to synthesize telechelic polymers by reacting the nitroxide end-group with a maleimide-functionalized terpyridine unit in a post-polymerization process.[31] Despite the proven efficacy of the dynamic metal-ligand coordination bond for the preparation of linear supramolecular polymers, the formation of these structures is still under statistical control. In the formation of AB diblock copolymers, a two-step approach is used. First, the metal of choice is complexed with the end-group of the first block, A. Then, the second block, B, is complexed with the remaining metal binding sites to form the final diblock copolymer. The presence of terpyridine units on both blocks introduces statistical control to these systems, resulting in some inevitable contamination by A and B diblock homopolymers, though likely in minimal amounts.

Recent developments in dynamic organo- and hydrogels based on metal-ligand coordination have significantly enhanced the understanding of the thermodynamics and kinetics of these dynamic bonds and their impact on the viscoelasticity of polymer networks. Such dynamic systems exploit the binding capabilities of, for example, histidine, catechol and bisphosphonate ligands which in many occasions have been incorporated to the chain ends of multi-arm star polyethylene glycol, PEG, leading to polymer network precursors of well-defined functionality and molecular weight.[32] A particular limiting aspect of metal-ligand coordination is associated with the use of metal ions themselves. While the previous materials have been successfully formed in water and can even assemble into higher-order structures like micelles, the presence of metal ions restricts their application in many aqueous systems where low toxicity is a common factor.

Macrocyclic host-guest complexation is another interesting and extensively utilized approach for achieving dynamic covalent bonding. In the context of this review, such a complex or bond occurs when a guest molecule is trapped within the structure of a host. The latter usually features external functional groups that interact with solvent molecules, while its internal structures facilitate guest binding through a specific shape or a favorable environment. This is especially true for highly stable host-guest complexes where a hydrophobic guest is encapsulated into the hydrophobic cavity of a particular host, such as cyclodextrins (α-, β- and γ-CD) and cucurbit[n]urils, CB[n] ($n = 5 - 8$ and 10), in water through favorable solvophobic interactions (Figure 6). The macrocyclic-based host-guest complexation associated with flexible crown ethers typically exhibit K_a values ranging from 10^2 to 10^4 M^{-1} in polar organic solvents.[33] The CD host family displays relatively high K_a values, reaching up to 10^5 M^{-1} in water.[34,35] Remarkably, some members of the CB[n] host family have demonstrated even higher K_a values, in some cases up to 10^{12} M^{-1} in water.[36,37] Dynamic bonding *via* macrocyclic host-guest complexation is highly tunable based on the architecture, size and structural features of both the host and guest molecules, as well as dipole-dipole and ion-dipole interactions between them –given that the guest is often a charged species. Relevant cavity-bearing molecules include crown ethers, CDs, CB[n], and pillar[n]arenes among others (Figure 6).



γ-Cyclodextrin

Cucurbit[8]uril

Pillar[5]arene
perhydroxylated

Dibenzo-24-crown-8-ether

Figure 6: Structures of selected macrocycles.

Each type of macrocyclic host possesses unique characteristics, making the selection of the appropriate host for a specific reconfigurable system or polymeric materials dependent on the desired behavior of the final dynamic material. As will be discussed later, there are many opportunities to fine-tune the responsiveness of dynamic materials through host-guest complex formation.

A number of crown ethers varying in size have been prepared including bis(*p*-phenylene)-34-crown-10 (BPP34C10), bis(*m*-phenylene)-32-crown-10 (BMP32C10), dibenzo-24-crown-8 (DB24C8), and benzo-21-crown-7 (B21C7). While crown ethers exhibit relatively low K_a values, they have been exploited to produce a wide variety of structurally dynamic materials.[38,39] In general, the ring sizes of crown ethers can significantly affect the binding affinity for specific guest molecules. BPP34C10 and its derivatives can form a 1:1 threaded structure with 4,4'-bipyridinium derivatives (**2** in Figure 7b, for example),[40] a binding ability which inspired the development of a large family of catenanes and other mechanically interlocked systems based on cyclobis(paraquat-*p*-phenylene), CBPQT^{4+}.[41] BPP34C10 also exhibits relatively strong binding affinity for other dicationic species and more electron-deficient guests, such as 2,7-diazapyrenium derivatives (such as **3** in Figure 7b).[42] Owing to their molecular structure, BMP32C10 and its derivatives can interact with 4,4'-bipyridinium-containing guests, forming sandwich-like or threaded host-guest complexes.[43] DB24C8 and dibenzylammonium salts spontaneously form 1:1 host-guest complexes. Additionally, DB24C8 exhibits a 1:1 complexation stoichiometry with 4,4'-bipyridinium derivatives, though with a weaker binding affinity.[44] B21C7, the smallest benzo crown ether, forms host-guest complexes with secondary ammonium salts, showing a relatively high K_a.[45] On account of the outstanding host-guest binding capabilities of crown ethers, a broad array of crown ether-based dynamic bonds have been utilized to create supramolecular polymers characterized by diverse structural architectures including poly[*c*2]daisy linear structures, hyperbranched polymers, crosslinked networks, dendrimers, and star-shaped polymers.[38,46]

CDs are some of the most extensively studied and well-developed macrocyclic hosts, largely due to their straightforward synthesis and the ease with which the hydroxyl groups at the portal and periphery of their cavity can be functionalized.[35] Consequently, this facilitates their integration into various molecular systems, including polymeric materials. CD is easily synthesized through the enzymatic degradation of starch, making it commercially affordable and promising for industrial and biological applications. A key limitation of CD systems, however, is their relatively low affinity for specific guest molecules, which constrains the performance of their associated supramolecular materials. A wide range of dynamic hydrogels, stimuli-responsive coatings, and functional biomaterials have been developed utilizing CD host-guest interactions as dynamic bonds, with further details available in comprehensive reviews.[34,35,47,48]

Calixarene and pillararene derivatives generally exhibit much higher binding affinities with specific molecular guests compared to crown ethers and CDs.[49,50] They are also relatively easy to synthesize and functionalize. However, their strong association is primarily limited to certain metal ions. While these macrocycles have been integrated into sensing devices and polymer networks, the narrow range of stable host-guest complexes may limit their broader application in other fields.[51]

The CB[n] family shows significantly higher association levels in aqueous media compared to earlier macrocycles, making them highly promising for developing materials with exceptional physical properties.[36,37] However, a major drawback has been the limited functionalization methods and the difficulties in separation and purification. Recent advancements, though, have simplified the functionalization of CB[n],[52,53] marking a potential paradigm shift in its applications and unlocking opportunities to create materials with unprecedented properties.[54]

The basic structure of CB[n] is depicted in Figure 7a. It is a symmetric, barrel-shaped cyclic oligomer of glycoluril containing between 5 and 10 repeat units –other larger CB[n]s, including CB[14], have been identified but the CB[n] series with $n = 5 - 8$ and $n = 10$ are the most commonly used hosts. The tunable size of its hydrophobic cavity along with its polar carbonyl portals lead to exceptional encapsulation capabilities (*vide infra*). The CB[n] family shows distinct solubility trends that follow an odd-even pattern, which may be linked to changes in the arrangement of hydrogen-bonded water clusters around the homologues in water. CB[5] and CB[7] have relatively high solubilities of 20–30 mM in neutral water, whereas CB[6] and CB[8] display much lower solubilities of ca. 0.01–0.02 mM. Due to these properties, each member of the CB[n] family requires distinct approaches for separation and use in chemical reactions and molecular recognition. Methods for synthesizing, separating, and purifying CB[n] and its derivatives are still evolving, with recent efforts focused on isolating and scaling up functionalized CB[n] analogues, including both cyclic and open-chain species.[55,56] Since Mock and co-workers first demonstrated the ability of CB[6] to bind a series of alkylammonium and alkydiammonium ions in aqueous formic acid,[57,58] interest in the area of CB[n] complexation has grown significantly. Combining the fundamentals of CB[n] host-guest chemistry with the dimensional diversity within this macrocycle family has revealed a vast, previously unexplored realm of supramolecular chemistry.

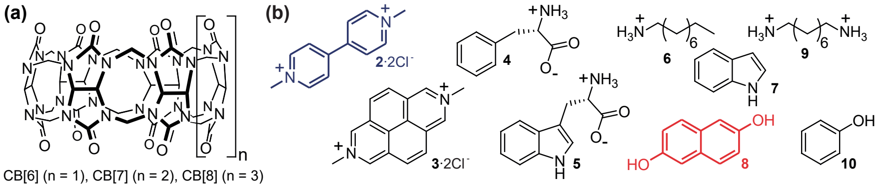


Figure 7: Structures of CB[6–8] (a) and selected guests **2**–**10** (b) including a common complementary pair of guest molecules, methyl viologen dichloride (**2**) and 2,6-dihydroxynaphthalene (**8**), leading to CB[8] heteroternary complexation.

In CB[5] to CB[7], only a single molecular species can be encapsulated. However, in CB[8] and larger homologues, the significantly larger cavity sizes enable the simultaneous binding of two guests (Figure 8a). This ability to form ternary inclusion complexes expands the possibilities for molecular recognition and interaction. CB[8], in particular, has been widely studied for its specific molecular recognition capabilities.[59] It exhibits strong affinities for small, flat aromatic guests, especially in three-component systems (i.e. ternary complex), where two guests are accommodated simultaneously inside the CB[8] cavity.[60,61] The guest-binding mechanism of CB[8] occurs in a stepwise manner. First, a 1:1 binary complex forms between CB[8] and an electron-deficient aromatic molecule (**2** or **3** in Figure 7b, for example), characterized by a relatively high association constant (K_a ca. $10^5 - 10^7\,\mathrm{M}^{-1}$). This is followed by a second binding event with an electron-rich, flat aromatic molecule (**7**, **8** and **10** in Figure 7b, for example). While the formation of the ternary complex has a slightly lower association strength, it still results in a thermodynamically stable three-component system with a high overall association constant (Figure 8a). A wide range of guest molecules involved in this or similar processes has been extensively studied by several research groups, including those led by Professors Kim, Nau, Isaacs, Scherman, Brunsveld, Buschmann, and Urbach.[62] A key focus within the CB[n] research community has been to understand CB[8] complex formation in water, as it is essential for creating dynamic materials with versatile, real-world applications.[63]

The initial exploration of ternary CB[8] complexation in supramolecular polymer chemistry was conducted by Scherman and co-workers. Their work focused on preparing end-functional polymers that incorporated specific complementary guests for CB[8].[64,65] Subsequently, the use of this macrocycle as the mediating linker, a hierarchy of self-assembling structures was produced (Figure 8). Diblock copolymers were successfully assembled by combining a polymer bearing a single first guest with CB[8] and an analogous polymer with a second guest (Figure 8c).[64,66] Furthermore, if the block lengths are designed strategically, taking into account the balance of hydrophobicity and hydrophilicity, it becomes possible to achieve higher-order structures such as cylindrical micelles and polymer vesicles. Another example is the use of functional side-chain homopolymers to produce dynamic hydrogels.[67,68] In this approach, complementary polymer chains with pendant guest molecules were prepared. Specifically, two polymers were synthesized: one with first guest moieties and the other with second guest moieties (Figure 8d). When these polymers are combined in specific ratios with CB[8], they form a three-dimensional crosslinked hydrogel that can retain significant amounts of water, with some hydrogels achieving water content as high as 99.95%.[69] This exceptional water retention reduces the required amount of hydrogelator while also providing shear-thinning and self-healing characteristics. Other reconfigurable materials exploiting the binding capabilities of CB[8] include microcapsules and polymer micelles as substance delivery systems,[70] crystalline two-dimensional fibers,[71] stimuli-responsive colloids,[72] and protein hybrids,[73] among others.

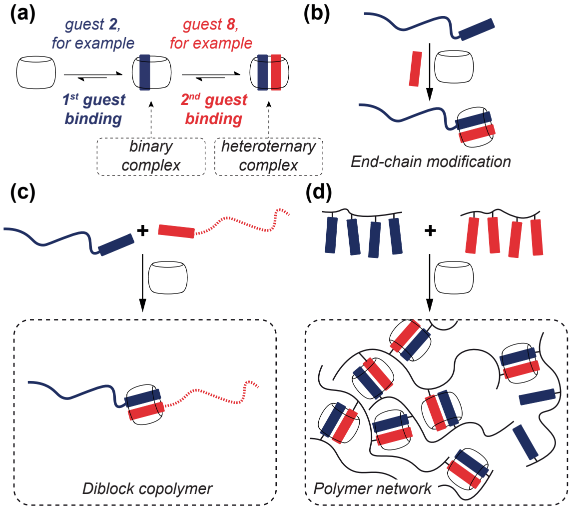


Figure 8: Schematic representation of the formation a CB[8] heteroternary complex (a) and a series of structurally dynamic polymer constructs based on CB[8] complexation: end-modified linear homopolymer (b), diblock copolymer (c) and polymer network (d).

The progress in supramolecular chemistry has allowed for the development of materials forming robust yet dynamic non-covalent materials. It is apparent that a new research area has solidified a place in the field of polymer science, as the materials that have been produced possess many of the important and well-known properties of traditional covalent polymers, yet offer the opportunity for responsiveness to external stimuli.

1.2 Dynamic covalent interactions

Dynamic covalent chemistry can be seen as a synthetic strategy that combines the robustness of covalent bonds with the adaptability of dynamic interactions. Indeed, it involves the reversible formation and breaking of covalent bonds leading to the creation of molecular systems that can respond to changes in their environment in a predictable manner.[74,75] Most traditional covalent synthetic transformations pursue the formation of new bonds which are created to be static and permanent under normal standard conditions. Conversely, dynamic covalent chemistry relies on covalent bonds that can form and dissociate reversibly. Such a process is usually achieved through the equilibrium between different molecular states, and it is typically governed by thermodynamic control, meaning that the system tends to reach the most thermodynamically stable state.[76] Indeed, this feature allows the system to (i) adapt in response to external stimuli –including pH and temperature changes, or the presence of specific chemical species– and (ii) even self-heal after damage (*vide infra*).

Examples of reversible covalent bonds in dynamic covalent chemistry include imine bonds, boronic esters, and hydrazones, among others (Figure 9). Like the previously mentioned non-covalent interactions (see Section 1.1), these dynamic covalent bonds have been integrated with various organic building blocks to develop materials for applications such as tissue regeneration, drug delivery, and sensors among others.[77]

While thermodynamic control is crucial, the kinetics of bond formation and breaking also play a significant role. Some dynamic covalent bonds can exchange at ambient temperatures, but many exhibit exchange rates that are extremely slow, resulting in, for example thermally gated stress relaxation behaviour (*vide infra*). For some systems, it has been

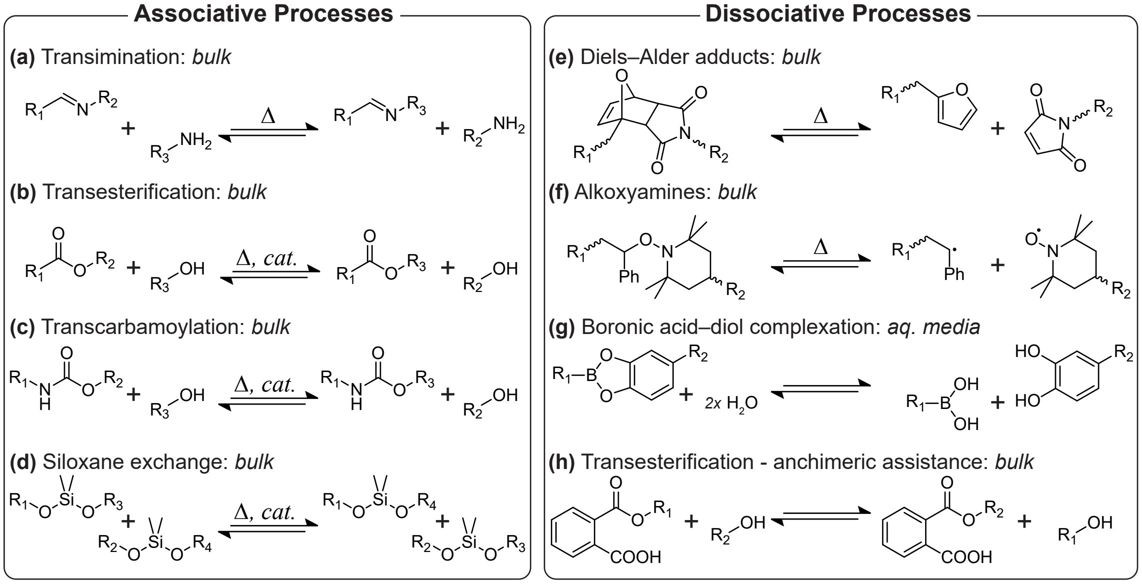


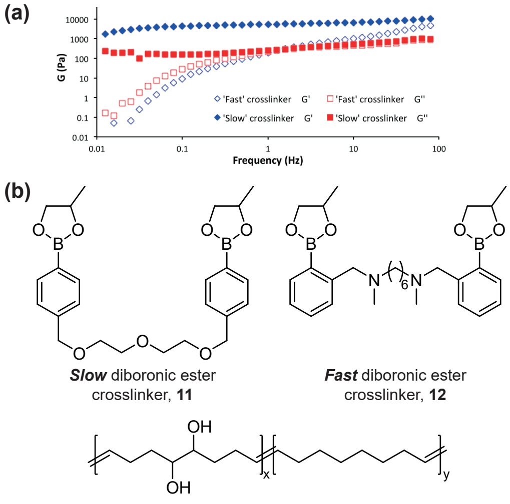
Figure 9: Selected examples of associative and dissociative dynamic covalent interactions.

suggested that bond lifetimes between 1 millisecond and 1 minute provide connections that are stable and detectable with most analytical methods, while still being dynamic enough to enable rapid adaptation.[78] This results in equilibrium times ranging from hours to days for large dynamic systems. Concerning the practical applications of (macro)molecular materials that incorporate dynamic covalent bonds, the maximum equilibration time is related to the stability of the system, as equilibrium must be achieved before any significant uncontrolled degradation occurs. Since covalent connections are in general more stable than supramolecular interactions, dynamic covalent bonds tend to be more robust but also exchange more slowly compared to their non-covalent counterparts. Therefore, most dynamic covalent bonds necessitate elevated temperature and/or the presence of a catalyst to facilitate exchange (Figure 9).

In the context of dynamic covalent materials, mild reaction conditions are beneficial for preserving bond integrity and maintaining sensitive non-covalent interactions within the system. The specific dynamic covalent bond must also align with the intended application, with resistance to moisture and oxygen being generally crucial. In biological applications, a dynamic covalent bond should exchange readily in water (Figure 9g, for example); however, only a few bonds that meet these criteria have been identified.

It is important to note that, quite often, there is a trade-off between stability and equilibration rates, as more reactive dynamic covalent bonds typically result in decreased system stability and *vice versa*. Indeed, the use of a catalyst to facilitate equilibration is quite common in dynamic covalent materials. The catalytic species can be manipulated to halt equilibration before analysis or to selectively toggle the exchange on or off. A diverse array of bond exchange catalysts has been employed with dynamic covalent materials, ranging from simple buffered acid or base solutions to complex multicomponent catalytic systems. Several of these approaches will be discussed in the following sections. The list of chemistries that have been used in dynamic covalent materials formation is broad, and include transesterification, Diels-Alder cycloaddition, boronic ester complexation, etc. These dynamic covalent molecular systems continuously break and reform bonds in response to physical or chemical cues such as mechanical loading, pH, or temperature. This adaptability leads to the development of highly processable, self-healing materials with frequency-dependent mechanical properties. For instance, disulfide motifs were recognized early on as reversible.[79] More recently, the reversible formation and cleavage of disulfide bonds in response to light and pH was utilized to create dynamic hydrogels.[80,81] Another common strategy to produce dynamic covalent materials involves the incorporation of acylhydrazone binding motifs in dynamic linear polyamides to reversibly exchange repeating monomers.[82] Schiff's base chemistry has also been utilized to create crosslinkable and self-healable polymer networks through imine or hydrazine bond formation in aqueous media. For instance, Wei and co-workers reported an injectable hydrogel suitable as a biocompatible carrier for specific cell therapy applications.[83] Alternatively, boronic ester formation takes place under mild conditions in aqueous media, notably without requiring a catalyst (see Figure 9g). Indeed, boronic ester exchange is possible even under physiological conditions.[84] Additionally, the reactivity of boronic acids with diol species can be modified through various strategies, such as neighboring group effects, enabling the preparation of materials with tunable mechanical properties (Figure 10).[85,86]

Overall, the chemistries and strategies for preparing dynamic covalent polymeric materials are diverse, each with its own thermodynamics and kinetics, resulting in varying macroscopic responses to external stimulation.[87,88] A few selected examples of such strategies have been presented in this section, with additional information available in recent com-



Slow diboronic ester crosslinker, **11**

Fast diboronic ester crosslinker, **12**

1,2-diol-containing polycyclooctene polymer, **13**

Figure 10: Rheological behavior (a), G' (diamonds) and G" (squares), of samples of polymer **13** (b) crosslinked with diboronic esters **12** (open symbols) and **11** (closed symbols). Adapted with permission from ref 86. Copyright 2015 American Chemical Society.

prehensive reviews.[89,90] The following sections focus on the implications of incorporating dynamic bonds into polymer materials, their sensitivity to external stimuli and recent trends.

2 Thermally-responsive structurally dynamic polymers

Many stimuli-responsive materials with dynamic bonds, particularly those utilizing non-covalent binding motifs, inherently exhibit thermoresponsive behavior due to the relative weakness of these interactions. The sensitivity to thermal stimuli depends on factors such as the type of dynamic bond integrated into polymeric systems and whether it is part of the main chain or acts as a side-chain crosslinking moiety. These strategies, commonly used to facilitate heat-driven reorganization of polymer structures after synthesis, have been extensively studied to impart properties like self-healing, improved processability, and controlled viscoelasticity.[91]

One interesting supramolecular polymer network exhibiting self-healing behavior relies on multiple donor–acceptor π–π stacking interactions.[92,93] Such material is comprised of a physical mixture of a polyamide equipped with terminal pyrene groups and a copolyimide bearing π-electron-deficient diimide moieties in the main chain of the polymer. The mixture of these two polymer results in a physical blend capable of producing free-standing films with remarkable tensile modulus of up to 1 MPa at 30 °C. The enhanced mechanical properties of the blend are attributed to the intercalation of the terminal electron-rich pyrene moieties of the polyamide into the chain folds of the polyimine containing multiple electron-deficient diimide moieties. The association of these complementary components is thermally reversible, allowing the material to heal itself (Figure 11). In fact, damaged films can be restored and regain their original tensile modulus by briefly heating to 80 °C. This healing capacity is reproducible across multiple cycles without a loss of efficiency.

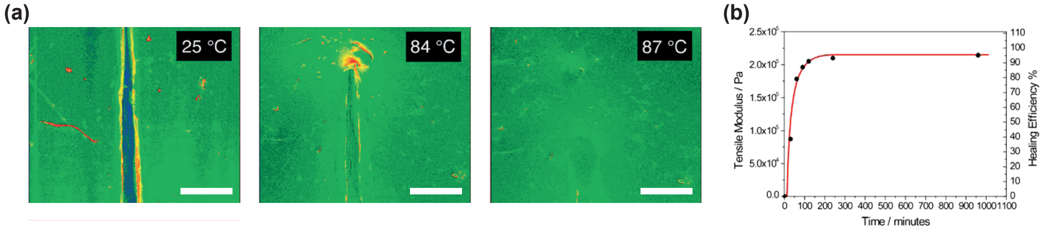


Figure 11: SEM images (scale bars: 300 μm) demonstrating the thermally-induced self-healing behavior of a supramolecular polymeric material (a) and recovery of tensile modulus as a function of healing time (b). Adapted with permission from ref 93. Copyright 2010 American Chemical Society.

In addition to donor–acceptor π–π stacking interactions, hydrogen bonding and other types of non-covalent interactions,[94, 95] a wide variety of healable materials have been implemented by exploiting reversible covalent bonds including Diels-Alder adducts,[96] dynamic covalent alkoxyamine bonds[97] and disulfides[98, 99] to name just a few. Indeed, in the past decade, the field of thermoresponsive dynamically reconfigurable materials has experienced substantial growth, leading to the emergence of a new materials, among which covalent adaptable networks, CANs, stand out prominently. CANs combine the advantageous properties of thermosets and thermoplastics. They exhibit the mechanical strength and solvent resistance of thermosets while maintaining the ability to be reprocessed and reshaped like thermoplastics. This unique combination is enabled by the presence of dynamic bonds, usually dynamic covalent bonds, which, similar to earlier examples, can break and reform under specific conditions, enabling the polymer network to rearrange without compromising its integrity.

Tobolsky and co-workers identified stress relaxation in covalent polymer networks in the 1940s during their investigations into the viscoelastic behavior of polysulfide rubbers and other polymeric materials.[79,100] At that time, the stress relaxation behavior was tentatively associated with the exchange of disulfide bonds. However, the concept of chemically induced stress relaxation remained largely unexplored for several decades until the 1990s and early 2000s, when it gained renewed interest with a focus on reprocessable and recyclable thermoset materials.[101,102] One important milestone in reprocessable materials is the introduction of vitrimers,[103] as one new family of CANs, by Leibler and co-workers in 2011.[104] The first vitrimer materials applied a zinc catalyst to introduce dynamic covalent transesterification into classical thermosetting epoxy–acid and epoxy–anhydride systems. At room temperature, the materials behave like standard thermosets and do not flow. However, thanks to the catalyst-accelerated transesterification of β-hydroxy esters present in the network, the system can change its topology through bond reshuffling above a characteristic temperature. Solubility tests conducted at high temperature demonstrated that the network is essentially insoluble even after prolonged immersion in a good solvent, thus confirming the *associative* nature of the exchange –in contrast to a *dissociative* mechanism (*vide infra*). Such associative reaction mechanism involves bond exchange reactions where a new bond forms before the old bond breaks, maintaining the crosslinked structure throughout the process (Figure 12a). These materials can flow above a second glass transition temperature, coined T_v, which can be seen as a topology freezing transition temperature. Creep-recovery and stress relaxation experiments indicate that these materials exhibit Arrhenius-like behavior regarding their viscosity. Such a behavior is controlled by dynamic covalent exchange reactions and can be tuned by varying the type and amount of catalyst. The materials proposed by Leibler and co-workers are readily repairable and can be reshaped by localized heating to achieve a new equilibrium shape, provided the duration of the application of stress exceeds the relaxation time at the specified temperature.[105,106]

Another type of CAN, introduced by Drockenmuller and co-workers, involves dynamic covalent transalkylation exchange of $C-N$ bonds.[107] In this case, poly(1,2,3-triazole)-containing networks were generated *via* the addition of an azide-alkyne monomer and a dibromo aliphatic species, without the use of solvent or catalyst. At elevated temperatures, the exchange between pendant halide functionalities and triazole rings enables complete stress

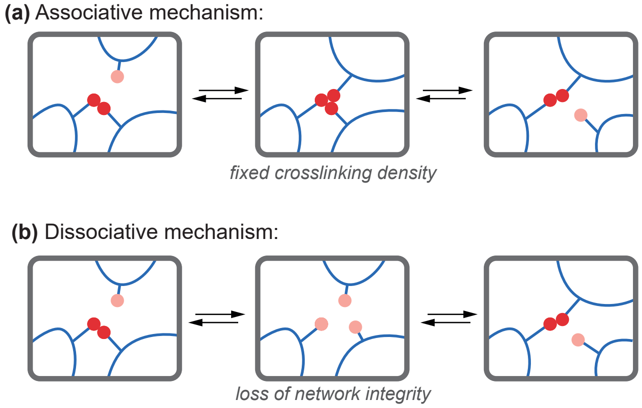


Figure 12: Schematic representations of associative (a) and dissociative (b) exchange reactions in structurally dynamic polymer networks.

relaxation. It was shown that the material can be reprocessed a number of cycles through a grinding compression molding process and even maintained its conducting properties after the reprocessing.

Leibler and co-workers have recently demonstrated that crosslinked polybutadiene can be turned into a material with vitrimer-like behavior by addition of a relatively low amount of Grubbs' second generation Ru catalyst.[108] Initially, an insoluble network was formed *via* radical-induced crosslinking of polybutadiene. The material was subsequently swollen in a good solvent to remove residual small molecule impurities through washing. After drying, the material was re-swollen in a Grubbs' catalyst solution. A control experiment was run whereby the catalyst was loaded into the material after being deactivated through cross-metathesis with an excess of vinyl ether, and both systems were investigated for their dynamic behavior. The authors demonstrated that the C−C metathesis catalyst facilitated exchange between the alkylidene catalyst and the double bonds in the polymer backbone, allowing for macroscopic flow. In cyclic creep-recovery experiments, the material exhibited continuous creep, with higher catalyst concentrations accelerating this phenomenon. Similar trends were observed at elevated temperatures and in stress relaxation experiments. In contrast, the control material with the deactivated catalyst showed no signs of creep or stress relaxation, confirming that the dynamic polymer reorganization is facilitated by the catalyst-mediated C−C metathesis. Recently, it has been demonstrated that dioxaborolane metathesis can be used to create vitrimers from commodity polymers including poly(methyl methacrylate), polystyrene, and high-density polyethylene. Despite being permanently crosslinked, the final polymer networks can be reprocessed multiple times through extrusion or injection molding.[109]

CANs are also capable of undergoing structural reorganization *via* a dissociative mechanism (Figure 12). Such a mechanism involve the temporary breaking of bonds within the network, leading to a transient decrease in crosslink density. Upon reformation of the bonds, the network is restored. Dissociative polymer networks have been reported using a variety of reversible covalent bonds such as Diels-Alder adducts, thioesters, dynamic urea bonds, Schiff's bases, boronic esters and boroxines.[90, 91] Wudl and co-workers developed a thermally remendable crosslinked polymeric material that behaves like traditional epoxy resins at standard operating temperatures. However, it can restore its properties after fracturing when heated to elevated temperatures.[110, 111] Wudl's material takes advantage of the relatively mild temperature and rapid equilibrium of the maleimide–furane Diels-Alder dynamic bond. Indeed, at 120 °C the degree of inactive crosslinks was determined to be around 30%. Upon cooling, the system was shown to recover its initial crosslinking degree. Similar materials, produced using a solvent-free method, were reported to achieve healing efficiencies exceeding 80%. An alternative approach were reported by Lehn and co-workers exploiting a bifunctional dicyanofumarate in the presence of ethylene glycol based bifunctional fulvenes.[112] This method generated dynamic polymers, ultimately leading to self-healing materials through the introduction of fulvene crosslinkers. The reader is referred to recent reviews for more details on CANs exhibiting a dissociative mechanism.[90, 91, 113]

In summary, structurally dynamic polymers have made use of a wide variety of thermally activated reversible bonds. Among the materials presented (*vide supra*), CANs represent a significant advancement in polymer science, offering a unique combination of properties from both thermosets and thermoplastics. Whether based on associative or dissociative mechanisms, reconfigurable polymer networks lead to materials with< dynamic, adaptable properties. As research progresses, the potential of CANs and other dynamic polymer networks continues to expand, paving the way for new innovations in materials science.[114]

3 Beyond thermoresponsive materials: Light- and chemoresponsive behaviors in structurally dynamic polymers

In addition to the thermally triggered behavior seen in structurally dynamic polymers (Section 2), these materials may also respond to chemical species or stimuli that alter the stability of dynamic bonds. Several dynamic bonds, such as Schiff's base chemistry, macrocyclic host-guest complexation, boronic esters, and disulfides have been utilized to create materials that respond to, for example, pH changes, redox stimuli or the presence of specific chemical species (Figure 1). In this context, light –in combination, many times, with specific photoswitches– serves as an efficient and clean stimulus that can act non-invasively, offering excellent spatiotemporal control through modulation of properties like wavelength, intensity, and polarization.[115] Using light to trigger the reorganization of polymeric structures eliminates the risks associated with undesirable thermally initiated processes, such as irreversible degradation of the polymer backbone. Additionally, light demonstrates a high degree of orthogonality with various chemical species and functionalities.[116] Light excitation can also induce the reversible formation of new covalent bonds, particularly through cyclization reactions –a phenomenon that has been extensively utilized for the patterning and structuring of polymeric systems.[117,118]

Reversible cycloaddition reactions represent a prominent category of bond-forming processes widely used in polymer chemistry and materials science. Among these, the $[2+2]$ photodimerization of cinnamates (Figure 13a) is one of the most commonly employed cyclization reactions. This reaction is frequently utilized to produce insoluble crosslinked systems, rendering these materials suitable for applications like photoresists. Over the past few decades, the area of cinnamate-functionalized materials has significantly expanded, and crosslinked cinnamate-containing polymers have been applied in a variety of fields including photoalignment layers for LCs,[119] stimuli-responsive hydrogels,[120] and reconfigurable –via a dissociative mechanism– polymer networks and elastomeric materials.[121]

Another light-induced bond formation reaction is the $[2+2]$ photodimerization of coumarin derivatives. This process produces the corresponding cyclobutane dimer upon irradiation with light of $\lambda > 300$ nm, and can be reversed using UV light with a shorter

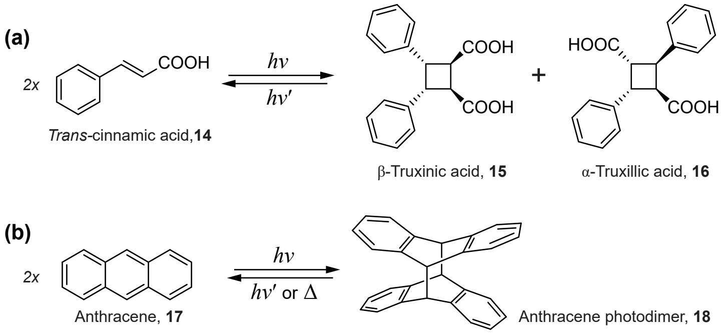


Figure 13: Examples of photoinduced cycloaddition reactions include *trans*-cinnamic acid (a) and anthracene (b). Figure illustrates two of the possible isomers formed from the photoinduced dimerization of *trans*-cinnamic acid.

wavelength. Similarly to cinnamate materials, coumarin-containing polymers have been used in LC photo-alignment,[122] and the development of a wide variety of patterned surfaces and stimuli-responsive materials,[123,124] including reconfigurable polymer networks.[125] In a recent study, Wu and colleagues demonstrated the use of the photodimerization of a coumarin derivative as a dynamic bond, creating a hydrogel by copolymerizing a coumarin-functionalized methacrylate monomer with acrylic acid in the presence of hexadecyltrimethylammonium chloride (CTAC) micelles (Figure 14).[126]

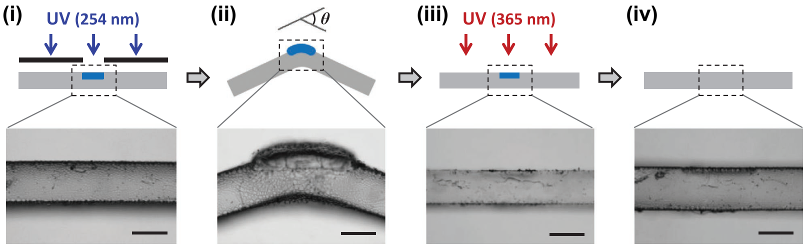


Figure 14: Schematic representation and images (i–iv) illustrating the reversible folding of a hydrogel strip controlled by light (scale bars: 500 μm). The sample is structured *via* a through-thickness light-induced sensitization process gradient with the aid of a photomask. Adapted with permission from ref 126. Copyright 2021 John Wiley & Sons, Inc.

The hydrogel exhibited a rewritable gradient structure owing to the presence of the photoresponsive coumarin functional moieties. The weakly charged poly(acrylic acid) formed a series of polyelectrolyte–surfactant complexes with CTAC, which increased the local concentration of coumarin moieties and, consequently, enhanced the dimerization efficiency. In addition, the polyelectrolyte–surfactant complexes served as physical crosslinkers to improve the mechanical performance of the hydrogel. Upon irradiation with 254 nm UV light, the coumarin dimers in the hydrogel cleaved, resulting in a swollen gel with a Young's modulus of 30 kPa. It was shown that the hydrogel can return to its original, more robust state, by first being exposed to an acidic aqueous solution and then irradiated with 365 nm UV light.

The photodimerization of anthracene is another well-established strategy for reversibly breaking and reforming covalent bonds through a photochemical reaction, following a dissociative mechanism similar to the previous examples in this section (Figure 13b). Many anthracene derivatives have the ability to photodimerize *via* a $[4+4]$ cycloaddition under excitation with UV light (λ of *ca.* 366 nm).[127] The resulting dimers, which increase the crosslinking degree of the antharacene-containing network, can be reverted thermally at relatively high temperatures (typically above 180 °C) or photochemically with UV light irradiation of $\lambda < 300$ nm. This phenomenon has been exploited to impart self-healing, recycling, and shape-memory behaviors in various polymer systems.[128] It is important to note that the reduced conjugated system and contorted geometry of the dimeric motifs –in comparison to the monomeric anthracene moieties– can per se significantly impact the photochromic and mechanical properties of the polymeric architecture they are incorporated to.[129]

In addition to the previous reactions, other photoinduced processes to reversibly reconfigure the structure of a polymer network at the molecular level include the photo-triggered radical mediated addition-fragmentation chain transfer (AFT), which is particularly attractive because of its relatively fast reaction kinetics. Similar to traditional reversible addition-fragmentation chain transfer (RAFT) reactions, AFT chemistry involving allyl sulfides combines the stability of covalent bonds with the reactivity typical of radical processes.[130,131] During this light-triggered process, each absorbed photon can initiate a series of bond exchanges, leading to rearrangement within the polymer network. However, the total number of cleaved bonds at any given moment remains relatively low. Bowman and co-workers have produced a series of polymer networks, *via* thiol–ene Click Chemistry, through the use of mixtures of di- and tetra-functional thiols and a reactive allyl sulfide derivative.[132] The resulting networks showed creep-recovery behavior upon irradiation with light of different wavelengths and demonstrated that AFT of allyl sulfides can be exploited to obtain dynamic materials. This concept has been further exploited for stress-managing in polymer glasses, composites and coatings.[133,134]

Matyjaszweski and co-workers have utilized trithiocarbonate and thiuram disulfide binding motifs to impart photoinduced dynamic behavior into a series of polymer networks (Figure 15).[135,136] Similar to processes in RAFT polymerization, both trithiocarbonate and thiuram disulfide groups can undergo reshuffling under UV and visible light irradiation, respectively, resulting in reversible bond rearrangement. Although trithiocarbonate-based materials exhibit self-healing properties, their applications may be limited due to the low stability of intermediate carbon radical species in air and at high temperatures, along with potential undesired recombination or termination processes. In contrast, thiuram disulfide materials demonstrate enhanced oxygen-tolerant self-healing capabilities.

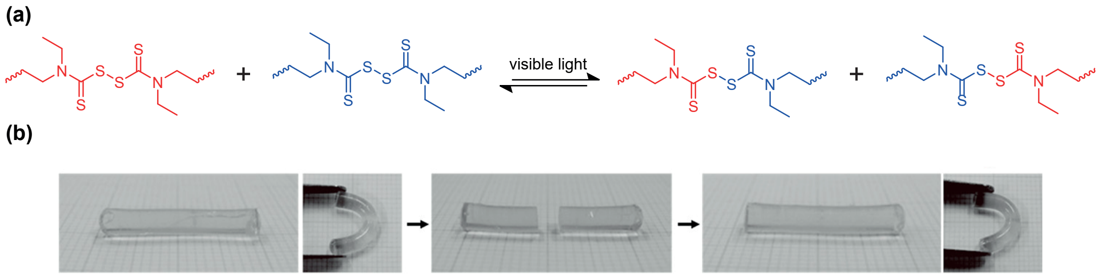
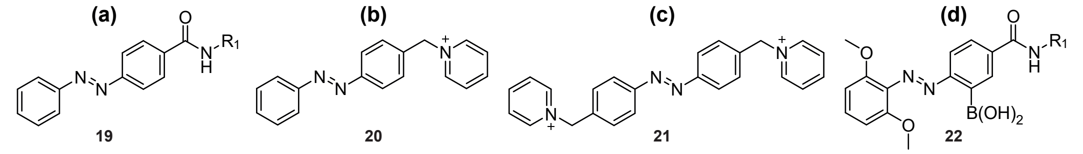


Figure 15: Visible light triggered shuffling of thiuram disulfide moieties (a) and self-healing (b). Adapted with permission from ref 136. Copyright 2012 John Wiley & Sons, Inc.

An alternative strategy for achieving photocontrol over structurally dynamic polymers involves the use of azobenzenes and other photoisomerizable moieties. Azobenzene is probably the most widely used class of photoswitches,[137] owing to its simple structure, rapid and straightforward synthesis, and robust and efficient photochemistry.[138,139] The photoinduced reversible isomerization of azobenzene derivatives results in significant changes in molecular geometry and polarity.[140] This phenomenon forms the basis for a wide variety of applications, ranging from optical data storage to photo-triggered substance release.[141,142] Indeed, azobenzene-containing materials, particularly liquid crystalline elastomers (LCEs) and networks, have been extensively studied over the past four decades for their use in light-controlled actuators and photodeformable materials.[7,143] In this regard, azobenzene converts light stimulation into specific deformations through a combination of photothermal and photochemical processes,[144] or primarily photochemical processes in some cases,[145] without the need for bond reshuffling. In some other cases, the isomerization of azobenzene is accompanied by a significant change in the connectivity of specific polymeric architectures. For instance, the complexation of CDs by azobenzene guests has proven highly valuable, as the binding constants of the E and Z isomers toward the macrocycle differ significantly (Figure16a).[146] Such a phenomenon has been exploited to produce, for example, photoresponsive CD-containing hydrogel actuators and light-responsive adhesives.[147,148]

In CB[n] systems, as previously introduced (Section 1.1), azobenzene derivatives have primarily been used as second guests in heteroternary complexes by attaching to a water-soluble moiety or polymer.[149,150] There is a report in which azobenzene derivatives, substituted with two quaternized amines, serve as first guests for CB[8].[151] The binding mode of these doubly charged derivatives to CB[8] is determined by the nature of the cationic group. Trimethylammonium substituents induce 1:1 complexation and allow for the uptake of a second guest (Figure 16b), while a pyridinium substituents induce a 2:2 binding mode (Figure 16c). Upon isomerization to the Z form, both molecules take a 1:1 binding mode and do not allow for the uptake of another guest, likely due to the larger volume occupied by this isomer. This represents and alternative strategy to remotely control the connectivity of polymeric systems by means of light irradiation. In the context of boronic ester complexation, Kalow and co-workers have recently demonstrated that ortho-azobenzene boronic acids exhibit isomerism-dependent binding equilibria with diols (Figure 16d).[152] Small differences in the binding affinity to diols significantly impact the dynamic boronic ester bonds that hold together polymeric networks (organogels). Indeed, the viscoelasticity of the gels can be remotely controlled with visible light, including red light. As our understanding of the isomerization of azobenzenes and other photoswitches expands, it is essential to comprehend how specific phototriggered isomerization processes occur in both solution and bulk materials, or in the presence of specific host molecules, as significant differences can exist in the photoresponsive behavior of a given photoswitch. This knowledge will help identify new opportunities for controlling the structure of soft materials, such as polymer networks, gels, and LCs, using light.



(a) **19** α-CD host-guest complexation
aq. buffer, UV/Vis light
ref. [146]

(b) **20** CB[8] host-guest complexation
aq. buffer, UV/Vis light
ref. [149]

(c) **21** CB[8] host-guest complexation
aq. buffer, UV/Vis light
ref. [151]

(d) **22** Boronic acid-diol complexation
DMSO and aq. buffer, green (525 nm) and red (626 nm) light
ref. [152]

Figure 16: Examples of incorporating azobenzenes into polymer constructs that result in light-responsive, structurally dynamic materials.

In addition to the thermal- and light-induced responsive behavior, another possible stimulation is the triggering associated with the chemical composition of the environment. In contrast to previously introduced examples, chemical stimulation offers unique advantages in terms of specificity, mild operating conditions, and versatility, particularly in complex and sensitive environments like biological systems.[153] While thermal and light stimuli are valuable for their ability to be externally applied and controlled, chemical stimuli excel in applications requiring selective, reversible, and energy-efficient responses. Their speed can range from fast (seconds to minutes) to slow (hours) depending on the kinetics of chemical reaction involved, the concentration and diffusion rates of the triggering species, and the polymer architecture among other aspects. Nonetheless, chemical responses are generally slower than the typical rapid reactions triggered by light in dynamic polymeric materials. As already mentioned, the triggering associated with changes in pH is indeed quite frequent, as pH sensitivity is inherent to many dynamic bonds including imines and Coulombic interactions.[83] Beyond pH, disulfide bonds, for example, can undergo reversible exchange reactions under redox conditions.[98] In the presence of a reducing agent, such as glutathione, disulfide bonds switch to thiols, which can revert back to disulfides bond under oxidative conditions. Additionally, boronic acids can react with diols to form boronic esters, and this reaction is reversible depending on the pH and the presence of competing diols (for example, specific monosaccharides such as glucose).[154] These transformations occur under thermodynamic control, ensuring that the dynamic bonds respond appropriately to changes in the environment.

One less explored mechanism in chemoresponsive structurally dynamic polymers is the induction of specific conformational changes through the reversible formation and cleavage of dynamic binding motifs. A notable example of this is an LCE developed by Rowan and co-workers that incorporates metal ion-binding sites derived from 2,6-bis(2-benzimidazolyl)pyridine (Bip).[155] In the absence of metal ions, the Bip-derived binding motifs adopt a rod-like conformation and, overall, the crosslinked material exhibits liquid crystal (LC) behavior. In the presence of metal ions (Fe^{2+}), however, the Bip-derived binding motifs form metal-ligand complexes causing a large rearrangement of the polymer network and the loss of the LC properties. Such a LC-to-isotropic transition upon metal ion binding, in well-aligned monolithic samples, forms the basis for actuation, and enables functions such as weight lifting. It was also demonstrated that various metal ions, including those from transition metals and lanthanide salts, can serve as effective actuation triggers. These actuation mechanisms could be utilized in controlled substance delivery systems and sensing devices for parameters such as humidity, metal ions, and pH.

4 Outlook and conclusions

Our capability to develop dynamic binding chemistries and apply them in polymer science with ease and precision is crucial for creating innovative materials that can respond predictably to specific stimuli, self-heal, adapt, or even be programmed to perform multiple tasks. Such properties are highly relevant in a number of contexts including chemical recyclability,[156] soft robotics,[157] and energy conversion and storage.[158] Breakthroughs in these areas will of course be the result of a multidisciplinary collaboration among chemists, physicists, and engineers each contributing to the complex puzzle of materials innovation. Progress will be driven by both industrial and societal demands –such as the need to rethink polymer design and manufacturing for effective reuse, waste collection, and recycling– as well as by curiosity-driven research. As the field of structurally dynamic polymers continues to evolve, it is essential to deepen and strengthen our fundamental understanding of the complex behavior of dynamic bonds, CANs and supramolecular materials –a know<ledge that not only underpins existing technologies,[159, 160] but also drives the development of new applications and materials.[161] A notable example is the broad family of "flowable" crosslinked polymers (Section 2). These materials behave like conventional thermosets under serving (or operating) conditions but can be reprocessed like thermoplastics when a chemical reaction, such as bond exchange, is activated (primarily by heat). Nevertheless, for practical industrial applications, bond exchange should be a highly activated and rapid reaction during polymer processing to prevent degradation –at temperatures of 200 to 250 °C typically– while, at the same time, remain sufficiently slow, or even dormant, under normal operating conditions to suppress creep. Such a challenge, already recognized in pioneering reports,[162] has been at the focus of substantial theoretical and experimental research effort for the last 50 years. Examples of creep resistant yet dynamic polymer networks are beginning to appear (see Section 2). Some of them achieve their properties by managing the availability of catalysts or additives that are external to the composition of

the polymer networks. Additionally, the presence of common functional groups within the polymer architecture, located in spatial proximity to specific dynamic or covalent bonds, can significantly influence chemical exchange. This phenomenon, known in organic chemistry as neighboring group participation (NGP),[163] has become an exciting design concept for tuning reactive bonds and controlling the dynamic behavior of dynamic covalent networks.[104] Our group has exploited in the past the benefits of NGP effects to develop a diverse range of LC materials.[164,165] Currently, one of our main focuses is the reversible condensation of *ortho*-substituted aryl aldehydes/ketones boronic acids (Figure 17a) and amines, and α-effect amines (nucleophiles including hydrazides and aminooxy derivatives). Quantitative condensation takes place in aqueous media, at mM concentrations and neutral pH, when a boronic acid group is in close proximity (*ortho* position) to the carbonyl group of the electrophile.[166,167] The remarkable stability of these adducts is associated with specific interactions between the electron-rich imine nitrogen and the electron deficient boron. The imine adduct **23** depicted in Figure 17b exhibits a K_d (observed) of ca. 10 mM in aqueous media (pH 7.0). In contrast, the imine formed from the condensation of 2-methoxy-1-ethanamine and 3-formylphenylboronic acid –analogous to **23**, but without any NGP effects– exhibits a much higher K_d of about 5 M, indicating significantly lower stability.[168] Since the association constants (K_a values fall in the $10^2 - 10^7\,\mathrm{M}^{-1}$ range depending on the pair of nucleophile and electrophile, see adducts **23**–**25** in Figure 17) and kinetics (typical k_{on} values in the $10^2 - 10^3\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ range) of boron-stabilized imine adducts at physiological pH cover a wide spectrum range, we believe the potential for material properties tunability is exceptional. Our aim is to explore this dynamic bond for the development of tunable viscoelastic hydrogel –designed for use as injectable local drug delivery systems and adaptable cell niches– as well as polymeric micelles and DNA-polymer hybrid materials.

Expanding our fundamental understanding of dynamic bond behavior, whether in aqueous media or in bulk –with the former being especially relevant for biomedical applications– will be essential for improving the design of dynamic polymer materials and tackling challenges in, for example, biomedicine[169,170] and plastic recycling.[156] Indeed, it has been shown that commodity polymers can be modified with dynamic covalent bonds to enable reprocessing, enhance upcycling of waste products, or recover the material value of individual plastics with ease.[109,171,172]

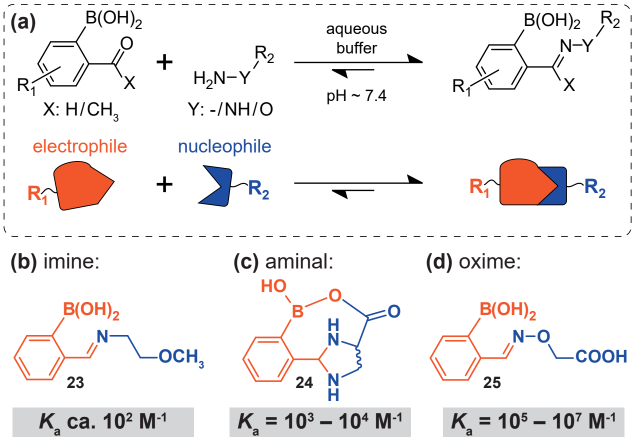


Figure 17: Ortho-substituted aryl aldehyde boronic acids react rapidly (k_{on} ca. $10^2 - 10^3$ $\mathrm{M}^{-1}\mathrm{s}^{-1}$) with amine-based nucleophiles in neutral aqueous media (a) to yield stable yet reversible adducts (b–d).

In addressing biomedical challenges, the integration of both dynamic bonds (such as host-guest complexation) and reactive bonds (e.g., acrylate groups) within the same polymeric structure presents a particularly promising strategy for creating synthetic surrogates of the natural extracellular matrix or viscoelastic inks for 3D printing in tissue engineering.[173] Polymer networks incorporating covalent and dynamic bonds –supramolecular or dynamic covalent– have also proven particularly valuable in creating hydrogels with extreme toughness,[174] as well as glassy gels that are transparent and rigid like Plexiglas® while also being stretchy, adhesive, self-healing, and electrically conductive.[175,176] Such crosslinked networks could become significant in energy storage and soft robotics, where there is a demand for robust, dynamic, and multifunctional materials.[177] Additional areas that could benefit from the use of structurally dynamic polymers include underwater adhesives and sealants,[178] responsive coatings,[179,180] haptics,[181] additive manufacturing,[182,183] smart textiles,[184] and more.

A key takeaway is that the thoughtful integration of dynamic bonds into polymeric constructs, such as networks, block copolymers and polymeric micelles, creates valuable structurally dynamic materials. This concept is illustrated in this brief review through selected examples and research projects, including several conducted in Zaragoza. While some aspects and trends –such as the use orthogonal binding chemistries,[185] transient dynamic binding in non-equilibrium systems,[186] and the development of dynamic polymers activated by mild stimuli like visible or near-infrared (NIR) light,[187,188] which are essential for biological and medical applications– are only briefly discussed, the selected examples high-light significant progress in the field over the past few years and underscore the crucial role that the dynamic bonds will continue to play in advancing future materials and polymer technologies.

Acknowledgements

I would like to sincerely thank the Real Academia de Ciencias de Zaragoza for selecting me as the recipient of the Premio de Investigación 2024 en la Sección de Químicas. Although this award is individual, it reflects the contributions of many who have played a key role in my education and a significant part of the research outlined in this review. I feel fortunate to work alongside such talented and dedicated individuals. I am indebted to Luis Oriol, Carlos Sánchez and Oren Scherman, for their mentoring and support throughout my PhD, postdoctoral, and senior research stages, as well as sparking my interest in polymer chemistry and self-assembly. I extend my thanks to my PhD students Enrique Guerreiro, Alejandro Postigo, Mehrzad Javadzadeh, Joseba Ruiz, Rahul Singh Yadav, Santiago Sarasa and María Sofía Navarrete for their effort and commitment. Additionally, I am thankful to the Liquid Crystals and Polymers group for their continued support, with special appreciation to Silvia Hernández, whose contributions have been deeply enriching and extend far beyond our scientific collaboration.

I would like to thank my host research institutions in Spain, including Universidad de Zaragoza and Instituto de Nanociencia y Materiales de Aragón, INMA (CSIC- Universidad de Zaragoza). I also thank the support from Gobierno de Aragón and Ministerio de Ciencia, Innovación y Universidades, as well as from my industrial partners, Schlumberger and Certest Biotec. Over the past seven years, my research activity in Zaragoza has been made possible through various projects: RYC-2015-18471, CTQ2017-84087-R, PID2020-113003GB-I00, CNS2022-135887, PCI2023-143390 and the Marie Skłodowska-Curie Innovative Training Network STORM-BOTS.

References

[1] C.S. Brazel, S.L. Rosen, *Fundamental Principles of Polymeric Materials*, Wiley, 2012.

[2] H. Staudinger, *Ber. Dtsch. Chem. Ges.* 1920, **53**, 1073–1085.

[3] W. Zhang, Y. Jin, Dynamic Covalent Chemistry: *Principles, Reactions, and Applications*, Wiley, Hoboken, 2017

[4] S. Samanta, S. Kim, T. Saito, A.P. Sokolov, *J. Phys. Chem. B* 2021, **125**, 9389–9401.

[5] S.J. Rowan, S.J. Cantrill, G.R.L. Cousins, J.K.M. Sanders and J.F. Stoddart, *Angew. Chem., Int. Ed.*, 2002, **41**, 898–952.

[6] S.J.D. Lugger, S.J.A. Houben, Y. Foelen, M.G. Debije, A.P.H.J. Schenning, D.J. Mulder.*Chem. Rev.* 2022, **122**, 4946–4975.

[7] T. White, D. Broer, *Nat. Mater.* 2015, **14**, 1087–1098

[8] R.J. Wojtecki, M.A. Meador, S.J. Rowan, *Nat. Mater.* 2011, **10**, 14–27.

[9] L. Brunsveld, B.J.B. Folmer, E.W. Meijer, R.P. Sijbesma, *Chem. Rev.* 2001, **101**, 4071–4097.

[10] A. Ciferri, *Supramolecular Polymers*, Taylor and Francis Group: New York, 2005

[11] R.B. Martin, *Chem. Rev.* 1996, **96**, 3043–3064.

[12] P.J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, 1953.

[13] C.G. Odian, *Principles of Polymerization*, Wiley: New York, 2004.

[14] A. Ciferri, *Macromol. Rapid. Commun.* 2002, **23**, 5111–529.

[15] M.E. Cates, *Macromolecules* 1987, **20**, 2289–2296.

[16] M. . Cates, *J. Phys. Chem.* 1990, **94**, 371–375.

[17] R.P. Sijbesma, F. H.Beijer, L. Brunsveld, B. J.B. Folmer, J.H.K.K. Hirschberg, R.F.M. Lange, J.K.L. Lowe, E.W. Meijer, *Science* 1997, **278**, 1601–1604.

[18] M.J. Krische, J.-M. Lehn, *The Utilization of Persistent H-Bonding Motifs in the Self-Assembly of Supramolecular Architectures*, Springer, 2000.

[19] R.P. Sijbesma, E.W. Meijer, *Chem. Commun.* 2003, **1**, 5–16.

[20] E.A. Appel, J. del Barrio, X.J. Loh, O.A. Scherman, *Chem. Soc. Rev.* 2012, **41**, 6195–6214.

[21] S.H.M. Söntjens., R.P. Sijbesma, M.H.P. van Genderen, E.W. Meijer *J. Am. Chem. Soc.* 2000, **122**, 7487–7493.

[22] X. Yang, F. Hua, K. Yamato, E. Ruckenstein, B. Gong, W. Kim, C. Y. Ryu, C.Y. *Angew. Chem. Int. Ed.* 2004, **43**, 6471–6474.

[23] D.A. Leigh, C.C. Robertson, A.M.Z. Slawin, P.I.T. Thomson, *J. Am. Chem. Soc.* 2013, **135**, 9939–9943.

[24] Y. Sun, J. Gu, H. Wang, J.L. Sessler, P. Thordarson, Y.-J. Lin, H. Gong, *J. Am. Chem. Soc.* 2019, **141**, 20146–20154.

[25] R.F.M. Lange, M.V. Gurp and E.W. Meijer, *J. Polym. Sci., Part A: Polym. Chem.*, 1999, **37**, 3657–3670.

[26] B.J.B. Folmer, R.P. Sijbesma, R.M. Versteegen, J.A.J. van der Rijt, E.W. Meijer, E.W. *Adv. Mater.* 2000, **12**, 874–878.

[27] O.A. Scherman, G.B.W. Ligthart, H. Ohkawa, R.P. Sijbesma, E.W. Meijer, E.W. *Proc. Natl. Acad. Sci. U.S.A.* 2006, **103**, 11850–11855.

[28] R. Hogg, R.G. Wilkins, *J. Chem. Soc.* 1962, 341–350.

[29] M. Heller and U.S. Schubert, *Macromol. Rapid Commun.* 2001, **22**, 1358–1363.

[30] B.G.G. Lohmeijer, U.S. Schubert, *J. Polym. Sci., Part A: Polym. Chem.* 2003, **41**, 1413–1427.

[31] B.G.G. Lohmeijer, U.S. Schubert, *J. Polym. Sci., Part A: Polym. Chem.* 2004, **42**, 4016–4027.

[32] L. Shi, P. Ding, Y. Wang, Y. Zhang, D. Ossipov, J. Hilborn, *Macromol. Rapid Commun.* 2019, **40**, 1800837

[33] G.W. Gokel, W.M. Leevy, M.E. Weber, *Chem. Rev.* 2004, **104**, 2723–2750.

[34] K.A. Connors, *Chem. Rev.* 1997, **97**, 1325–1358.

[35] M.V. Rekharsky, Y. Inoue, *Chem. Rev.* 1998, **98**, 1875–1918.

[36] J. Lagona, P. Mukhopadhyay, S. Chakrabarti, L. Isaacs, *Angew. Chem. Int. Ed.* 2005, **44**, 4844–4870

[37] S.J. Barrow, S. Kasera, M. J. Rowland, J. del Barrio, O.A. Scherman *Chem. Rev.* 2015, 115, 12320-12406.

[38] B. Zheng, F. Wang, S. Donga, F. Huang, *Chem. Soc. Rev.* 2012, **41**, 1621–1636.

[39] Z. Duan, F. Xu, X. Huang, Y. Qian, H. Li, W. Tian, *Macromol. Rapid Commun.* 2022, **43**, 2100775.

[40] B.L. Allwood, N. Spencer, H. Shahriari-Zavareh, J.F. Stoddart and D.J. Williams, *J. Chem. Soc., Chem. Commun.* 1987, 1064–1066.

[41] P.R. Ashton, T.T. Goodnow, A.E. Kaifer, M.V. Reddington, A.M.Z. Slawin, N. Spencer, J.F. Stoddart, C. Vicent and D.J. Williams, *Angew. Chem., Int. Ed. Engl.* 1989, **28**, 1396–1399.

[42] M. Liu, X. Yan, M. Hu, X. Chen, M. Zhang, B. Zheng, X. Hu, S. Shao, F. Huang, *Org. Lett.* 2010, **12**, 2558–2561.

[43] C. Yao, J. Zhang, M. Cheng, Q. Sun, Y. Pan, J. Jiang, L. Wang, *Macromol. Rapid Commun.* 2018, **39**, 1700218.

[44] S. Dong, Y. Luo, X. Yan, B. Zheng, X. Ding, Y. Yu, Z. Ma, Q. Zhao, F. Huang, *Angew. Chem. Int. Ed.* 2011, **50**, 1905–1909.

[45] J. Chen, X. Yan, X. Chi, X. Wu, M. Zhang, C. Han, B. Hu, Y. Yu, F. Huang, *Polym. Chem.* 2012, **3**, 3175–3179.

[46] Q. Chena, K. Zhu, *Chem. Soc. Rev.* 2024, **53**, 5677–5703.

[47] E.M. Martin del Valle, *Process Biochem.* 2004, **39**, 1033–1046.

[48] Z. Liu, Y. Liu, *Chem. Soc. Rev.* 2022, **51**, 4786–4827.

[49] A. F. D. de Namor, R. M. Cleverley, M. L. Zapata-Ormachea, *Chem. Rev.* 1998, 98, 2495-2526.

[50] T. Ogoshi, T. Yamagishi, Y. Nakamoto, *Chem. Rev.* 2016, **116**, 7937–8002.

[51] D. Xia, P. Wang, X. Ji, N.M. Khashab, J.L. Sessler, F. Huang, *Chem. Rev.* 2020, **120**, 6070–6123.

[52] D. Lucas, T. Minami, G. Iannuzzi, L. Cao, J. B. Wittenberg, P. Anzenbacher Jr., L. Isaacs, *J. Am. Chem. Soc.* 2011, **133**, 17966–17976.

[53] M. M. Ayhan, H. Karoui, M. Hardy, A. Rockenbauer, L. Charles, R. Rosas, K. Udachin, P. Tordo, D. Bardelang, O. Ouari, *J. Am. Chem. Soc.* 2015, **137**, 10238–10245.

[54] H. Yin, Q. Cheng, D. Bardelang, R. Wang, *JACS Au* 2023, **3**, 2356–2377.

[55] B. Vinciguerra, L. Cao, J. R. Cannon, P. Y. Zavalij, C. Fenselau, L. Isaacs, *J. Am. Chem. Soc.* 2012, **134**, 13133–13140.

[56] L. Isaacs, *Acc. Chem. Res.* 2014, **47**, 2052–2062.

[57] W.L. Mock, N.Y. Shih, *J. Org. Chem.* 1983, **48**, 3618–3619.

[58] P. Balaram, *ACS Omega* 2024, **9**, 4162–4165.

[59] K. Kim, *Chem. Soc. Rev.* 2002, **31**, 96–107.

[60] H.-J. Kim, J. Heo, W. S. Jeon, E. Lee, J. Kim, S. Sakamoto, K. Yamaguchi, K. Kim, K. *Angew. Chem. Int. Ed.* 2001, **40**, 1526–1529.

[61] M.E. Bush, N.D. Bouley, A.R. Urbach, *J. Am. Chem. Soc.* 2005, **127**, 14511–14517.

[62] E. Masson, X. Ling, R. Joseph, L. Kyeremeh-Mensaha, X. Lu, *RSC Adv.* 2012, **2**, 1213–1247.

[63] J. Murray, K. Kim, T. Ogoshi, W. Yao, B.C. Gibb, *Chem. Soc. Rev.* 2017, **46**, 2479–2496.

[64] U. Rauwald, O.A. Scherman, *Angew. Chem. Int. Ed.* 2008, **47**, 3950–3953.

[65] U. Rauwald, J. del Barrio, X.J. Loh, O.A. Scherman, *Chem. Commun.* 2011, **47**, 6000–6002.

[66] X.J. Loh, J. del Barrio, P.P.C. Toh, T.-C. Lee, D. Jiao, U. Rauwald, E.A. Appel, O.A. Scherman, *Biomacromolecules* 2012, **13**, 84–91.

[67] E.A. Appel, F. Biedermann, U. Rauwald, S.T. Jones, J.M. Zayed, O.A. Scherman, *J. Am. Chem. Soc.* 2010, **132**, 14251–14260.

[68] C.S.Y. Tan, J. del Barrio, J. Liu, O.A. Scherman, *Polym. Chem.* 2015, **6**, 7652–7657.

[69] E.A. Appel, X J. Loh, S.T. Jones, F. Biedermann, C.A. Dreiss, O.A. Scherman, *J. Am. Chem. Soc.* 2012, *134*, 11767–11773.

[70] J. Zhang, J.; R.J. Coulston, S.T. Jones, J. Geng, O.A. Scherman, C. Abell, *Science* 2012, **335**, 690–694

[71] J. del Barrio, J. Liu, R.A. Brady, C.S.Y. Tan, S. Chiodini, M. Ricci, R. Fernández-Leiro, C.-J. Tsai, P. Vasileiadi, L. Di Michele, D. Lairez, C. Toprakcioglu, O.A. Scherman, *J. Am. Chem. Soc.* 2019, **141**, 14021–14025.

[72] Y. Lan, Y. Wu, A. Fox, O.A. Scherman, *Angew. Chem. Int. Ed.* 2014, **53**, 2166–2169.

[73] H.D. Nguyen, D.T. Dang, J.L.J. van Dongen, L. Brunsveld, *Angew. Chem. Int. Ed.* 2010, **49**, 895–898.

[74] S. J. Rowan, S.J. Cantrill, G.R. Cousins, J.K. Sanders, J.F. Stoddart, *Angew. Chem., Int. Ed.* 2002, **41**, 898–952

[75] F.B.L. Cougnon, A.R. Stefankiewicz, S. Ulrich, *Chem. Sci.* 2024, **15**, 879–895.

[76] P.T. Corbett, J. Leclaire, L. Vial, K.R. West, J.-L. Wietor, J.K.M. Sanders, S. Otto, *Chem. Rev.* 2006, **106**, 3652–3711.

[77] Y. Jin, C. Yu, R.J. Denman, W. Zhang, *Chem. Soc. Rev.* 2013, **42**, 6634–6654

[78] Y. Zhu, H. Yang, Y. Jin, W. Zhang, *Chem. Mater.* 2013, **25**, 3718–3723.

[79] M.D. Stern, A.V. Tobolsky *J. Chem. Phys.* 1946, **14**, 93–100.

[80] B.D. Fairbanks, S.P. Singh, C.N. Bowman, K.S. Anseth, *Macromolecules* 2011, **44**, 2444–2450.

[81] K.N. Plunkett, M.L. Kraft, Q. Yu, J.S. Moore, *Macromolecules* 2003 **36**, 3960–3966

[82] W.G. Skene, J.-M.P. Lehn, *Proc. Natl. Acad. Sci.* 2004, **101**, 8270–8275.

[83] B. Yang, Y. Zhang, X. Zhang, L. Tao, S. Li, Y. Wei, *Polym. Chem.* 2012, **3**, 3235–3238.

[84] J.N. Cambre, B.S. Sumerlin, *Polymer* 2011, **52**, 4631–4643.

[85] B. Marco-Dufort, M.W. Tibbitt, *Mater. Today Chem.*, 2019, **12**, 16–33.

[86] O.R. Cromwell, J. Chung, Z. Guan, *J. Am. Chem. Soc.* 2015 **137**, 6492–6495.

[87] P. Chakma, D. Konkolewicz, *Angew. Chem. Int. Ed.* 2019, **58**, 9682–9695.

[88] F. García, M.M.J. Smulders, *J. Polym. Sci. Part A: Polym. Chem.* 2016, **54**, 3551–3577.

[89] W.K. Zou, J.T. Dong, Y.W. Luo, Q. Zhao, T. Xie, *Adv. Mater.* 2017, **29**, 1606100.

[90] Z. Lei, H. Chen, S. Huang, L.J. Wayment, Q. Xu, W. Zhang *Chem. Rev.* 2024, **124**, 7829–7906.

[91] N. Zheng, Y. Xu, Q. Zhao, T. Xie, *Chem. Rev.* 2021, **121**, 1716-1745.

[92] S. Burattini, H.M. Colquhoun, J.D. Fox, D. Friedmann, B.W. Greenland, P.J.F. Harris, W. Hayes, M.E. Mackay, S.J. Rowan, *Chem. Commun.* 2009, 6717–6719.

[93] S. Burattini, B.W. Greenland, D. Hermida Merino, W. Weng, J. Seppala, H.M. Colquhoun, W. Hayes, M.E. Mackay, I.W. Hamley, S.J. Rowan *J. Am. Chem. Soc.* 2010 **132**, 12051–12058.

[94] L. Lewis, K. Stewart, M. Anthamatten, *Macromolecules* 2014, 47, 729-740.

[95] Y. Liu, L. Wang, L. Zhao, Y. Zhang, Z.-T. Li, F. Huang, *Chem. Soc. Rev.* 2024, 53, 1592-1623.

[96] B.J. Adzima, H.A. Aguirre, C.J. Kloxin, T.F. Scott, C.N. Bowman, *Macromolecules* 2008, 41, 9112–9117.

[97] H. Otsuka, K. Aotani, Y. Higaki, Y. Amamoto, A. Takahara, *Macromolecules* 2007, **40**, 1429–1434.

[98] R. Martin, A. Rekondo, A.R. de Luzuriaga, G. Cabanero, H.J. Grande, I. Odriozola, *J. Mater. Chem. A*, 2014, **2**, 5710–5715.

[99] C. King-Poole, H. Thérien-Aubin, *Adv. Funct. Mater.* 2024, 2405608.

[100] A.V. Tobolsky, *J. Appl. Phys.* 1956, **27**, 673–685.

[101] L. Leibler, M. Rubinstein, R.H. Colby, *J. Phys. II France* 1993, **3**, 1581–1590.

[102] T. Maeda, H. Otsuka, A. Takahara, *Prog. Polym. Sci.* 2009, **34**, 581–604.

[103] D. Montarnal, M. Capelot, F. Tournilhac, L. Leibler, *Science* 2011, **334**, 965–968.

[104] M. Guerre, C. Taplan, J.M. Winne, F.E. Du Prez, *Chem. Sci.* 2020, **11**, 4855–4870.

[105] M. Capelot, M.M. Unterlass, F. Tournilhac, L. Leibler, *ACS Macro Lett.*, 2012, **1**, 789–792

[106] M. Capelot, D. Montarnal, F. Tournilhac, L. Leibler, *J. Am. Chem. Soc.*, 2012, **134**, 7664–7667

[107] M.M. Obadia, B.P. Mudraboyina, A. Serghei, D. Montarnal, E. Drockenmuller, *J. Am. Chem. Soc.* 2015, **37**, 6078–6083.

[108] Y.-X. Lu, F. Tournilhac, L. Leibler, Z. Guan, *J. Am. Chem. Soc.* 2012, **134**, 8424–8427

[109] M. Röttger, T. Domenech, R. van der Weegen, A. Breuillac, R. Nicoläy, L. Leibler, *Science* 2017, **356**, 62–65.

[110] X. Chen, M.A. Dam, K. Ono, A. Mal, H. Shen, S.R. Nutt, K. Sheran, F. Wudl, *Science* 2002, **295**, 1698–1702

[111] X. Chen, F. Wudl, A.K. Mal, H. Shen, S.R. Nutt, *Macromolecules* 2003, **36**, 1802–1807.

[112] P. Reutenauer, E. Buhler, P.J. Boul, S.J. Candau, J.M. Lehn, *Chem. Eur. J.* 2009, **15**, 1893–1900.

[113] L. Li, X. Peng, D. Zhu, J. Zhang, P. Xiao, *Macromol. Chem. Phys.* 2023, **224**, 2300224.

[114] V. Zhang, B. Kang, J.V. Accardo, J.A. Kalow, *J. Am. Chem. Soc.*, 2022, **144**, 22358–22377

[115] M.-M. Russew, S. Hecht, *Adv. Mater.* 2010, **22**, 3348–3360.

[116] A. Goulet-Hanssens, F. Eisenreich, S. Hecht, *Adv. Mater.* 2020, **32**, 1905966.

[117] J. del Barrio, C. Sánchez-Somolinos, *Adv. Opt. Mater.* 2019, **7**, 1900598.

[118] T. Hughes, G.P. Simon, K. Saito, *Mater. Horiz.* 2019, **6**, 1762–1773.

[119] N. Kawatsuki, K. Goto, T. Kawakami, T. Yamamoto, *Macromolecules* 2002, **35**, 706–713.

[120] K. Takada, *Polym. J.* 2023, **55**, 1023–1033.

[121] H. Masai, T. Nakagawa, J. Terao, *Polym. J.* 2024, **56**, 297–307.

[122] M. Obi, S. Morino, K. Ichimura, *Macromol. Rapid Commun.* 1998, **19**, 643.

[123] A. Concellon, A.P.H.J. Schenning, P. Romero, M. Marcos, J.L. Serrano, *Macromolecules* 2018, **51**, 2349–2358.

[124] A. Concellón, P. Romero, M. Marcos, J. Barberá, C. Sánchez-Somolinos, M. Mizobata, T. Ogoshi, J.L. Serrano, J. del Barrio, *J. Org. Chem.* 2020, **85**, 8944–8951.

[125] S.A. Safavi-Mirmahalleh, M. Golshan, B. Gheitarani, M.S. Hosseini, M. Salami-Kalajahi, *Eur. Polym. J.* 2023, **198**, 112430.

[126] C.N. Zhu, C.Y. Li, H. Wang, W. Hong, F. Huang, Q. Zheng, Z.L. Wu, *Adv. Mater.* 2021, **33**, 2008057.

[127] H. Bouas-Laurent, J.-P. Desvergne, A. Castellan, R. Lapouyade, *Chem. Soc. Rev.* 2000, **29**, 43–55.

[128] J. Van Damme, F. Du Prez, *Prog. Polym. Sci.* 2018, **82**, 92–119.

[129] K.A. Günay, T.L. Ceccato, J.S. Silver, K.L. Bannister, O.J. Bednarski, L.A. Leinwand, K.S. Anseth, *Angew. Chem. Int. Ed.* 2019, **58**, 9912–9916.

[130] C.J. Kloxin, T.F. Scott, C.N. Bowman, *Macromolecules* 2009, **42**, 2551–2556.

[131] C.R. Fenoli, C.N. Bowman, *Polym. Chem.* 2014, **5**, 62–68.

[132] T.F. Scott, A.D. Schneider, W.D. Cook, C.N. Bowman, *Science* 2005, **308**, 1615–1617.

[133] T.F. Scott, R.B. Draughon, C.N. Bowman, *Adv. Mater.* 2006, **18**, 2128–2132.

[134] A.M. Mineo, M.E. Buck, R. Katsumata, *J. Polym. Sci.* 2021, **59**, 2719–2729.

[135] Y. Amamoto, J. Kamada, H. Otsuka, A. Takahara, K. Matyjaszewski, *Angew. Chem., Int. Ed.* 2011, **50**, 1660–1663.

[136] Y. Amamoto, H. Otsuka, A. Takahara, K. Matyjaszewski, *Adv. Mater.* 2012, **24**, 3975–3980

[137] F.A. Jerca, V.V. Jerca, R. Hoogenboom, *Nat. Rev. Chem.* 2022, **6**, 51–69.

[138] J.A. Delaire, K. Nakatani, *Chem. Rev.* 2000, **100**, 1817–1846.

[139] A. Natansohn, P. Rochon, *Chem. Rev.* 2002, **102**, 4139–4176.

[140] M. Sato, T. Kinoshita, A. Takizawa, Y. Tsujita, *Macromolecules* 1988, **21**, 1612–1616.

[141] S. Hvilsted, C. Sánchez, R. Alcalá, *J. Mater. Chem.* 2009, **19**, 6641–6648.

[142] J. del Barrio, L. Oriol, C. Sánchez, J.L. Serrano, A. Di Cicco, P. Keller, M.-H. Li, *J. Am. Chem. Soc.* 2010, **132**, 3762–3769.

[143] H.K. Bisoyi, Q.L. *Chem. Rev.* 2016, **116**, 15089–15166.

[144] A. Gelebart, A.D. Jan Mulder, M. Varga, A. Konya, G. Vantomme, E.W. Meijer, R.L.B. Selinger, D.J. Broer, *Nature* 2017, **546**, 632–636.

[145] P. Sartori, R.S. Yadav, J. del Barrio, A. DeSimone, C. Sánchez-Somolinos, *Adv. Sci.* 2024, **11**, 2308561.

[146] I. Tomatsu, A. Hashidzume, A. Harada, *J. Am. Chem. Soc.* 2006, **128**, 2226–2227.

[147] K. Iwaso, Y. Takashima, A. Harada, *Nat. Chem.* 2016, **8**, 625–632.

[148] A. Harada, Y. Takashima, M. Nakahata, *Acc. Chem. Res.* 2014, **47**, 2128–2140.

[149] J. del Barrio, P.N. Horton, D. Lairez, G.O. Lloyd, C. Toprakcioglu, O.A. Scherman, *J. Am. Chem. Soc.* 2013, **135**, 11760–11763.

[150] C.S.Y. Tan, J. del Barrio, J. Liu, O.A. Scherman, *Polym. Chem.* 2015, **6**, 7652–7657.

[151] J. del Barrio, S.T.J. Ryan, P.G. Jambrina, E. Rosta, O.A. Scherman, *J. Am. Chem. Soc.* 2016, **138**, 5745–5748.

[152] J.V. Accardo, E.R. McClure, M.A. Mosquera, J.A. Kalow, *J. Am. Chem. Soc.* 2020, **142**, 19969–19979.

[153] M. Gosecka, M. Gosecki, *Acta Biomater.* 2020, **116**, 32–66.

[154] V. Yesilyurt, M.J. Webber, E.A. Appel, C. Godwin, R. Langer, D.G. Anderson, *Adv. Mater.* 2016, **28**, 86–91.

[155] B.T. Michal, B M. McKenzie, S. . Felder, S.J. Rowan, *Macromolecules* 2015, **48**, 3239–3246

[156] M. Jiang, N. Mahmud, C.B. Koelbl, D. Herr, J.C. Worch, *J. Polym. Sci.* 2024, **62**, 3562–3583.

[157] Y. Chi, Y. Li, Y. Zhao, Y. Hong, Y. Tang, J. Yin, *Adv. Mater.* 2022, **34**, 2110384

[158] R. Liu, Z. L. Wang, K. Fukuda, T. Someya, *Nat. Rev. Mater.* 2022, **7**, 870–886.

[159] S.J. Harris, M.A. McKervey, D.P. Melody, J. Woods, J.M. Rooney, *Instant adhesive composition utilizing calixarene accelerators*, US 4556700 A, 1985.

[160] J. del Barrio, R.S. Hartshorne, T.L. Hughes, A. Meredith, *Viscosification of aqueous solutions*, US 11248162 B2, 2022.

[161] Note from the author: Both large multinational companies and smaller ventures, such as *SupraPolix B.V.*, *Cycladex Ltd.* and *Aqdot Ltd.*, which specialize in supramolecular materials, have demonstrated a keen interest in structurally dynamic polymers.

[162] P.C. Colodny, A.V. Tobolsky, *J. Am. Chem. Soc.* 1957, **79**, 4320–4323.

[163] B. Capon, Q. Rev., *Chem. Soc.*, 1964, **18**, 45–111.

[164] P. Cerrada, M. Marcos, J.L. Serrano, *Mol. Cryst. Liq. Cryst.* 1989, **170**, 79–87.

[165] M. Marcos, F. Navarro, L. Oriol, J.L. Serrano, *Makromol. Chem.* 1989, **190**, 305–311.

[166] P.M. Cal, J.B. Vicente, E. Pires, A.V. Coelho, L.F. Veiros, C. Cordeiro, P.M. Gois, *J. Am. Chem. Soc.* 2012, **134**, 10299–10305.

[167] P. Schmidt, C. Stress, D. Gillingham, *Chem. Sci.* 2015, **6**, 3329–3333.

[168] N.J. Gutiérrez-Moreno, F. Medrano, A.K. Yatsimirsky, *Org. Biomol. Chem.* 2012, **10**, 6960–6972

[169] A. Chrisnandy, D. Blondel, S. Rezakhani, N. Broguiere, M.P. Lutolf, *Nat. Mater.* 2022, **21**, 479–487.

[170] B.L. LeSavage, D. Zhang, C. Huerta-López, A.E. Gilchrist, B. A. Krajina, K. Karlsson, A.R. Smith, K. Karagyozova, K.C. Klett, M.S. Huang, C. Long, G. Kaber, C.M. Madl, P.L. Bollyky, C. Curtis, C.J. Kuo, S.C. Heilshorn, *Nat. Mater.* 2024, **23**, 1138-1149.

[171] E.G. Morado, M.L. Paterson, D.G. Ivanoff, H.-C. Wang, A. Johnson, D. Daniels, A. Rizvi, N.R. Sottos, S.C. Zimmerman, *Nat. Chem.* 2023, **15**, 569–577.

[172] R. W. Clarke, T. Sandmeier, K.A. Franklin, D. Reich, X. Zhang, N. Vengallur, T.K. Patra, R. J. Tannenbaum, S. Adhikari, S.K. Kumar, T. Rovis, E.Y.-X. Chen, *Nature* 2023, **616**, 731–739.

[173] A.P. Dhand, M.D. Davidson, J.H. Galarraga, T.H. Qazi, R.C. Locke, R.L. Mauck, J.A. Burdick, *Adv. Mater.* 2022, **34**, 2202261.

[174] X. Li, J.P. Gong, *Nat. Rev. Mater.* 2024, **9**, 380–398.

[175] Z. Huang, X. Chen, S. J.K. O'Neill, G. Wu, D.J. Whitaker, J. Li, J.A. McCune, O.A. Scherman, *Nat. Mater.* 2022, **21**, 103–109.

[176] M. Wang, X. Xiao, S. Siddika, M. Shamsi, E. Frey, W. Qian, W. Bai, B.T. O'Connor, M.D. Dickey, *Nature* 2024, **631**, 313–318.

[177] X. Liu, M. Gao, J. Chen, S. Guo, W. Zhu, L. Bai, W. Zhai, H. Du, H. Wu, C. Yan, Y. Shi, J. Gu, H.J. Qi, K. Zhou, *Adv. Funct. Mater.* 2022, **32**, 2203323.

[178] K. Kikkawa, Y. Sumiya, K. Okazawa, K. Yoshizawa, Y. Itoh, T. Aida, *J. Am. Chem. Soc.* 2024, **146**, 21168–21175.

[179] J. Sokjorhor, T. Yimyai, R. Thiramanas, D. Crespy, *J. Mater. Chem. B*, 2024, **12**, 6827–6839.

[180] K.D. Harris, C.W.M. Bastiaansen, J. Lub, D.J. Broer, *Nano Letters* 2005, **5**, 1857–1860.

[181] A. Gerald, S. Russo, *Nat. Rev. Mater.* 2024, **9**, 86–88.

[182] K. Yang, J.C. Grant, P. Lamey, A. Joshi-Imre, B.R. Lund, R.A. Smaldone, W. Voit, *Adv. Funct. Mater.* 2017, **27**, 1700318.

[183] D.J. Bischoff, M.E. Mackay, *ACS Appl. Polym. Mater.* 2024, 6, 3335–3341.

[184] H. Tan, L. Sun, H. Huang, L. Zhang, R.E. Neisiany, X. Ma, Z. You, *Adv. Mater.* 2024, **36**, 2310020.

[185] M.D. Preuss, T. Schnitzer, S.A.H. Jansen, S.C.J. Meskers, T.H.R. Kuster, X. Lou, E.W. Meijer, G. Vantomme, *Angew. Chem. Int. Ed.* 2024, **63**, e202402644

[186] A. Sorrenti, J. Leira-Iglesias, A.J. Markvoort, T.F. A. de Greef, T.M. Hermans, *Chem. Soc. Rev.* 2017, **46**, 5476–5490.

[187] A. Roche, E. Terriac, R.M. Tejedor, L. Oriol, A. del Campo, M. Piñol, *Eur. Polym. J.* 2020, **126**, 109561.

[188] D. Hoenders, S. Ludwanowski, C. Barner-Kowollik, A. Walther, *Angew. Chem. Int. Ed.* 2024, **63**, e202405582.